

Main Patterns of Geochemistry of Phosphorus

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Abstract

The paper presents the main conclusions of the Russian monograph “*Geochemistry of Phosphorus*” (2020). Based on statistical processing of ~6100 sample averages (from ~190,000 analyses), new estimations of World averages (Clarke values) for P_2O_5 , % (and P, %), phosphorus-titanium module (P_2O_5/TiO_2), phosphorus-calcium module (P_2O_5/CaO), phosphorus-iron module (P_2O_5/Fe_2O_3), and phosphorus-total iron module ($P_2O_5/Fe_2O_3 + FeO$). Many estimates have been made for the first time. In addition to the new Clarke estimates, sometimes very different from previous ones, the work carried out has led to a number of new conclusions. In particular, the titanium geochemical barrier for phosphorus has been first estimated, all the 11 genotypes of phosphogenesis have been named and characterized, five genetic correlations of phosphogenesis have been described, lithochemistry methods have been successfully applied to characterize the phosphorites. Due to the large breadth of generalization, the monograph has a large theoretical and applied value.

Keywords

Phosphorus, Geochemistry, Phosphorites, Lithochemistry, Clarke Values (World Average Contents)

1. Introduction

In the Soviet Union (before 1991) and post-Soviet Russia (after 1991), extensive research has been conducted on the geochemistry of phosphorus. The purpose of these studies was to develop scientific criteria for the search for the most important agronomic ores—phosphorites.

The most recent generalization of these studies was the fundamental monograph of Ya. E. Yudovich and two of his co-workers “*Geochemistry of Phosphorus*” (2020).

The criminal attack of the Russian government on democratic Ukraine led to

the fact that the whole Free World hated Russia, and at the same time—everything Russian...

Russian science, unfortunately, turned out to be one of the victims of this hatred: any connections between Western scientists and Russian researchers have become extremely limited. The consequence of this was the almost complete ignorance of Western researchers with this fundamental monograph on the geochemistry of phosphorus.

The purpose of this article is an attempt to correct the situation as much as possible.

After manganese and titanium, phosphorus is the last “small element” determined in the complete silicate analysis of rocks. But if in our book on the geochemistry of titanium [1] the biospheric processes of Ti concentration could be neglected without a big mistake, and in the book on the geochemistry of manganese [2] the role of such processes was recognized as important, but still not the most important, then the situation with the geochemistry of phosphorus is completely different. Along with carbon, phosphorus is the most important bioelement, without which life on our planet is impossible. Without phosphorus, the functioning of the mechanism of heredity (DNA, RNA), metabolism (ADP, ATP) and the existence of cells (phospholipids of cell membranes) are impossible, therefore, the biospheric aspect of phosphorus is so important that without it no full-fledged presentation of the geochemistry of this small element is impossible.

Another feature of the book being reviewed is the nature of the analyses used. The fact is that the bulk of the literature on phosphorus is devoted to *phosphate ores*: endogenous apatite, but mainly exogenous phosphorites, dominated by fluor-carbonate apatite, often called *francolite*. That is why a separate chapter 8 is devoted to phosphorites here, and extensive materials on the genesis of phosphorites are used in chapters 9 and 10.

For the rest, when preparing the refereed book, we used the already proven method of data collection and processing, described in detail earlier [1]. Statistical processing covered more than 6100 samples formed by us, covering about 190 thousand silicate analyses of rocks.

In the formed cluster samples, the average values (arithmetic and geometric) of all components and phosphorus modules, as well as their variances, were calculated. To characterize the three most important correlations of phosphorus (with titanium, iron and calcium), the following four modules were calculated:

PTiM—phosphorus-titanium module, P_2O_5/TiO_2

PCaM—phosphorus-calcium module, P_2O_5/CaO

PFeM—phosphorus-iron module, P_2O_5/Fe_2O_3

PFe(t)M—phosphorus-total iron module, $P_2O_5/Fe_2O_3 + FeO$

Sample averages by types of igneous, metamorphic and sedimentary rocks (for example, basites, meta-basites, sandy, clay, siliceous, etc.) were used to construct frequency histograms necessary for calculating Clarkes—similar to how we did it earlier in [1] [2] (Figure 1).

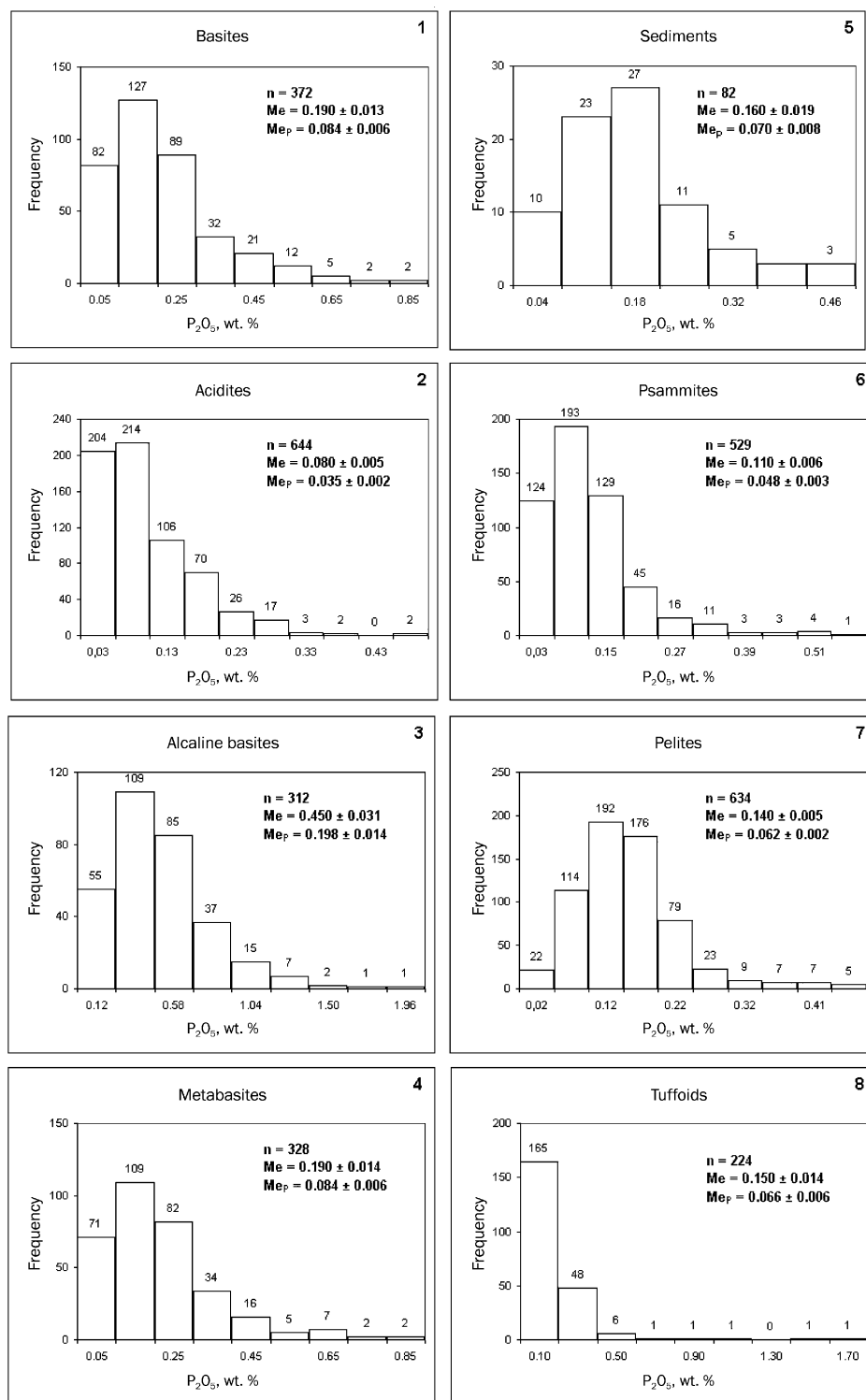


Figure 1. Examples of frequency diagrams for sets of analyses of hyperbasites (1), acidites (2), alkaline basites (3), meta-basites (4), sediments (5), psammites (6), pelites (7), tuffoids (8). Constructed according to A.I. Polyakov (1978), Ja.E. Yudovich (1981), V.I. Lennykh and L.T. Belyakova (1986), V.S. Popov and others (1987), L.D. Tugolesov *et al.* (1987), A.S. Byakov and K.A. Luneva (2006), V.I. Silaev (2008), A.V. Prokopyev and G.V. Ivensen (2008). In total, 30 such histograms are given in the monograph—both for P_2O_5 and for phosphorus modules for all types of rocks.

In the reviewed book, as before [1] [2], we defined Carke in the sets of analyses as the average median content. Since the vast majority of such sets do not correspond to the normal (Gaussian) distribution, the use of the value σ (mean square deviation) to determine the confidence 95% or 99% intervals around the mean value in the set becomes questionable. To determine 95% of the “near-Clarke interval” around the median, we use the formula of J. Chambers *et al.*¹:

$$Me \pm 1.57(Q_3 - Q_1) / \sqrt{N},$$

where Me is the median, Q_3 and Q_1 are the third and first quartiles, N is the sample size (in our case, the number of sample averages).

When interpreting the data of correlation analysis of P_2O_5 and phosphorus modules with components of silicate analysis, we, as before, considered geochemically significant only the values of correlation coefficients no worse than 5% significance level: $r \geq r_{0.05}$. All values of $r < r_{0.05}$ were not taken into account.

Correlation graphs were plotted for some significant phosphorus or phosphorus modules identified in this way (Figure 2).

2. Some General Information

This chapter of the monograph contains the information necessary for all subsequent chapters. The text of the chapter is compiled on the basis of major generalizations in geochemistry and mineralogy of phosphorus made in different years by our scientists: G.N. Baturin [3] [4], V.Z. Bliskovsky [5] [6] [7] [8], N.G. Brodskaya [9], I.I. Bok [10], O.V. Dudkin [11] [12], V.V. Ivanov [13], A.V. Kazakov [14], D.A. Mineev [8], V.S. Savenko [15], A.I. Smirnov [16], A.S. Sokolov [17], A.E. Fersman [18], A.L. Yanshin [19], so and a number of foreign specialists [20]-[25]. The materials considered and generalized by us earlier are also used; in particular, much is taken from the book devoted to geochemical and mineralogical indicators of lithogenesis [26].

All of the above allows us to draw some general conclusions:

1) For the concentration of phosphorus in the magmatic process, as first indicated by A.E. Fersman [18], the main importance is a rare combination of two factors: a) the attraction of phosphorus to volatile base (and not acidic) magmas and b) the association of phosphorus with residual volatile components (F, Cl, CO_2). Such a rare combination is realized in *alkaline base rocks*, the most famous representative of which is the multiphase, concentric-zonal Khibiny alkaline intrusion, whose ores contain an average of 47% apatite and 34% nepheline.

2) For many years, the attention of researchers (and, accordingly, a lot of publications) has been focused on isomorphic trace elements of phosphorites: uranium, strontium, rare earths and some others. For example, D.A. Mineev proved that the Khibiny phosphorous ores are simultaneously the largest deposit of rare earths. It was also found that the isotopic composition of phosphate oxygen, carbon and strontium can serve as an indicator of the genesis of phosphorites.

¹Chambers, John M., William S. Cleveland, Beat Kleiner, and Paul A. Tukey. Comparing Data Distributions//In Graphical Methods for Data Analysis, 62.—Belmont, California: Wadsworth International Group; 1983. ISBN 0-87150-413-8 International ISBN 0-534-98052-X.

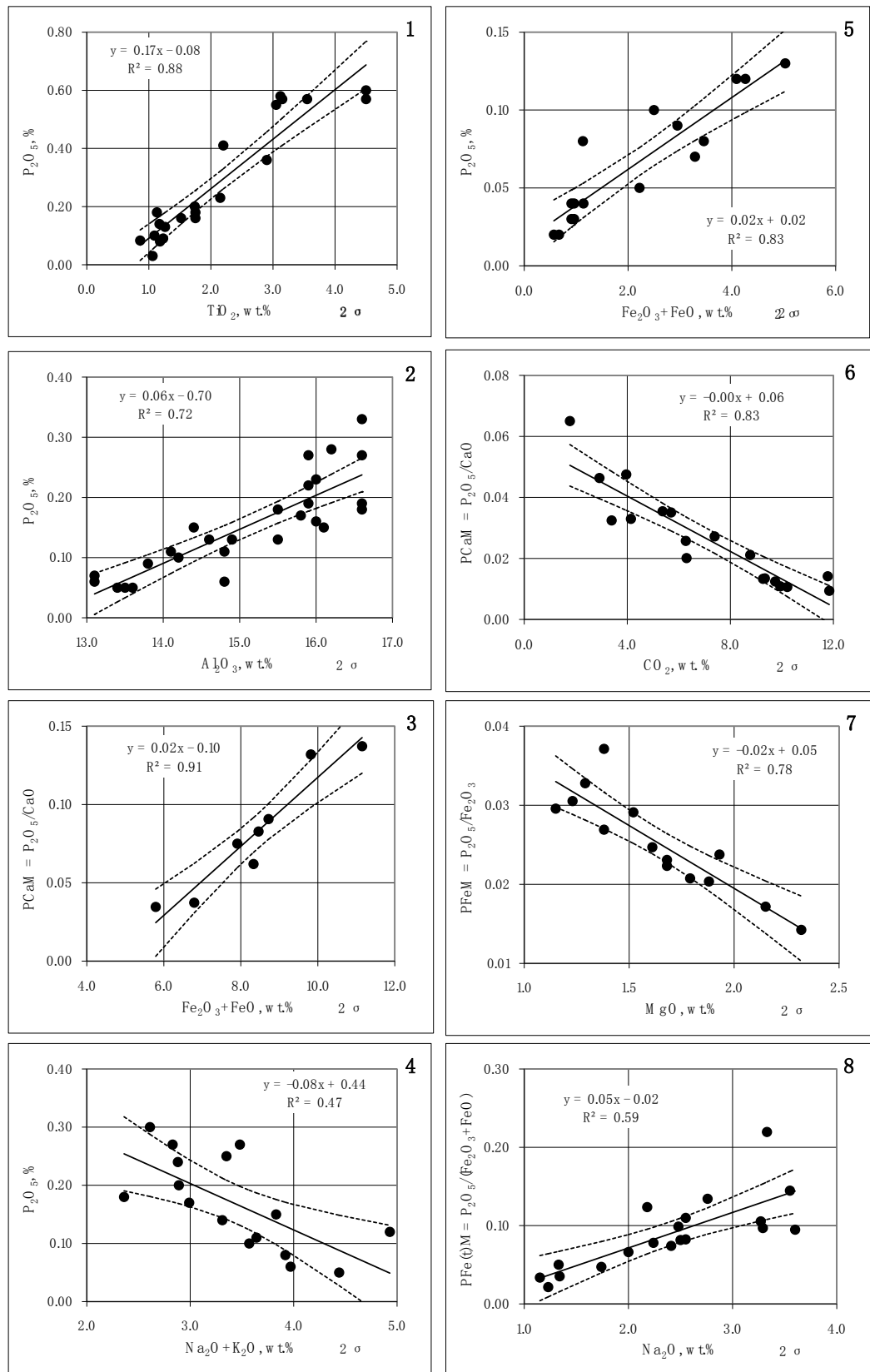


Figure 2. Examples of correlation graphs for the same sets of analyses as in **Figure 1**. In total, the mono-graph contains about 290 such graphs for all types of rocks.

3) The main geochemical barriers in phosphorus geochemistry are calcium and iron oxide, since phosphates Ca, Fe (II) and Fe (III) are poorly soluble. Very often these barriers (especially iron oxide) look like sorption; however, the processes of formation of stoichiometric compounds (chemisorption) are “behind the brackets” of sorption.

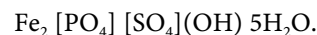
4) Ca-phosphate apatite is formed on the calcium geochemical barrier, which accounts for 96% of their total mass among the known 219 phosphates. Apatite has a general structural formula



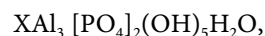
where A - Ca, as well as Sr, Ba, Pb, Ra, Na, etc.; X - P, as well as As, V, Si, S, C, etc.; Z - F, OH, Cl. Apatite is represented by three main varieties: endogenous high-temperature fluorapatite $Ca_{10} [PO_4]_6 F_2$, biogenic (skeletal) low-temperature hydroxyl-apatite $Ca_{10} [PO_4]_6 OH_2$ and hypergenic low-temperature carbonate-fluorapatite *francolite* $Ca_{10} [(PO_4)_{6-x}(CO)_x] (F, OH)_2$, which is often referred to simply as *carbonate-apatite*. It has long been established that fluorapatite is the least soluble in hypergenesis, whereas francolite is more soluble, the more the phosphate group in it is replaced by carbonate.

5) The main mineral of phosphorites—francolite—has the most complex composition with wide limits of isomorphic substitutions in both the cationic and anionic parts of the formula, therefore it is more rational to call the whole set of carbonatapatites—*francolites*, distinguishing among them the extreme members of isomorphic series with special names.

6) Al- and Ca-Al-phosphates such as *variscite*, *wavellite* and *crandallite* are formed in weathering crusts. At the same time, the specific sulfuric acid weathering of phosphate-containing sulfide-bearing black shales is characterized by aqueous iron sulfate *destinesite* (called in amorphous form *diadochite*) with the general formula

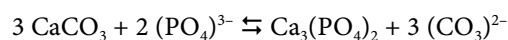


For tonsteins (volcanogenic kaolinite partings in coal seams), aqueous aluminophosphates with the general formula are very characteristic:



where the elements Sr (gojacite), Ba (gorseiskite), Ca ± U (florencite and its analogues) can be in position X.

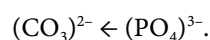
7) Under conditions of hypergenesis, the equilibrium between phosphate and calcium carbonate is very unstable, so that with slight fluctuations in pH and carbonate alkalinity (Alk), the equilibrium of the reaction



can easily shift in both directions, therefore, on the one hand, a Ca barrier is necessary for the formation of phosphorites in the sediment. In a substantially carbonate sediment, it already exists, and in a substantially terrigenous sediment, it occurs in diagenesis by concentration Ca in the nodules. On the other hand, an excess of calcium in the solution leads to an increase in carbonate alkalinity

(Alk) of silt waters, which leads to the dissolution of Ca phosphate. These two circumstances are the reason *for the enormous importance of diagenesis in the formation of phosphorites*, which was first reliably proved by G. N. Baturin in 1970 on the example of modern carbonaceous diatom sediments on the shelf of South Africa.

A very important type of Ca barrier is *metasomatic*, when phosphatization of a carbonate sediment or rock occurs, *i.e.* the carbonate group is replaced by a phosphate group:



The geological importance of this process lies in the fact that it is most likely due to the formation of the largest deposits of phosphorites in the carbonate strata of the Vendian-Cambrian and Upper Cretaceous-Paleogene.

8) On the iron-nitrous geochemical barrier, the aqueous phosphate of nitrous iron vivianite $\text{Fe}_3 [\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$ is formed, which is formed in the acidic reducing environment of modern peat bogs. The iron-oxide barrier in the sediment exists only under oxygen waters; in anoxic facies this barrier does not exist, and therefore a significant part of the primary biogenic phosphorus freely returns to the bottom water. The most obvious manifestation of the role of the iron-oxide barrier is the well-known paragenesis of phosphorites and glauconite, discussed in detail in chapter 10 of this book.

9) The most powerful geochemical barrier for phosphorus in conditions of hypergenesis is an organic barrier: living matter (LM). For example, plankton contains an average of 0.15% P_2O_5 , fish—about 4%, and animal bones—about 27%.

10) Another geochemical barrier for phosphorus—*titanium*, has escaped the attention of researchers. However, the reality of this barrier is proved by the correlation of phosphorus (or phosphorus modules) revealed on a huge analytical basis with titanium, which is discussed in detail in the following chapters of the monograph².

11) The most important regularity of the hypergenic geochemistry of phosphorus is the uneven distribution of phosphorus in ocean water vertically—a factor first emphasized by A.V. Kazakov in 1939 [14]. This is explained by the uptake of dissolved phosphorus in surface waters during photosynthesis (in the photic zone) and subsequent regeneration—the return of phosphorus to deeper waters during the death of both primary photosynthetics and animals participating in food chains. Therefore, the *phenomenon of upwelling* (the rise of deeper, phosphorus-enriched cold waters to the surface) provides intensive phosphorus uptake during plankton photosynthesis, which is of key importance in the hypergenic geochemistry of phosphorus.

12) Another important regularity of the ocean geochemistry of phosphorus is its accumulation in silt waters of the ocean sediments—the stronger the more

²See also: Yudovich Ya. E., Ketris M. P., Kotova O. B., Ponaryadov A. V., Rybina N. V. Titanium barrier in phosphorus geochemistry//Geochemistry, 2022, vol. 67, No. 6. P. 597-600.

C_{org} is buried in them, and therefore increasing from deep-sea red clays to coastal reduced sediments.

13) Another pattern is the *accumulation of phosphorus in the anoxic waters* of some water areas, for example, in the Black Sea. Some authors even considered this phenomenon to be the main reason for the formation of phosphorites.

14) Human activity, due to the widespread use of phosphorus fertilizers in agriculture, with the subsequent entry of phosphorus into river waters, has become a very significant factor in the biosphere phosphorus cycle.

3. Igneous Rocks

3.1. Hyperbasites

Following petrographic norms, igneous rocks containing SiO_2 from 30% to 45% were considered as *hyperbasites* (synonym—ultrabasites).

As can be seen in **Table 1**, the average median (approximately with a two-sigma deviation of the median) values of hyperbasite phosphateness calculated on the basis of 107 samples are 0.123 ± 0.031 for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively (or 0.054 ± 0.013 for elementary P), 0.20 ± 0.03 , 0.022 ± 0.003 , 0.026 ± 0.006 and 0.009 ± 0.003 . *These figures can be considered our Clarke estimates for hyperbasites.* Thus, the near-Clarke contents of P_2O_5 in normal (non-alkaline) hyperbasites fall within the range of 0.09% - 0.15%.

The new estimates of Clarke P are significantly lower than the estimates of R. Daly (1936)—0.016% and A.P. Vinogradov (1962)—0.017%. The reason is that in the calculation we excluded more phosphorous alkaline hyperbasites. This also applies to the estimate of the PTiM value obtained earlier ([1], p. 19), which was also overestimated (0.35 vs. 0.19), since samples with abnormal phosphorus contents were not excluded during the calculation.

Carbonatites both in their composition and genesis (essentially metasomatic?) form among hyperbasites a separate group. Using the example of a set of analyses of pre-tube carbonatites of Yakutia, the average median values of phosphateness (approximately with a two-sigma deviation of the median) are $0.74\% \pm 0.06\%$ for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively (or $0.33 \pm 0.03\%$ for elementary P), 0.59 ± 0.09 , 0.020 ± 0.003 , 0.022 ± 0.004 and 0.14 ± 0.01 . Thus, the average contents of P_2O_5 in pre-tube carbonatites are six times higher than in other hyperbasites, and the phosphorus-titanium module of PTiM is three times higher. The values of the phosphorus-calcium module (PCaM) are the same, and the modules with iron (PFeM and PFe(t)M) are an order of magnitude lower.

Kimberlites also form a separate group among hyperbasites. According to more than 580 analyses of kimberlite pipes from 14 districts of Yakutia ([27], p. 46), the average content of P_2O_5 in them is 0.55%, which is more than four times higher than our Clarke estimate of hyperbasites.

Table 1. Phosphorus content and values of phosphorus modules for igneous rocks.

Rocks	n	N	P ₂ O ₅ , %	P, %	PTiM	PCaM	PFeM	PFe(t)M
Hyperbasites	107	4172	0.123 ± 0.031	0.054 ± 0.013	0.197 ± 0.031	0.022 ± 0.003	0.026 ± 0.006	0.009 ± 0.003
Carbonatites	30	550	0.740 ± 0.063	0.326 ± 0.028	0.591 ± 0.092	0.020 ± 0.003	0.221 ± 0.037	0.136 ± 0.011
Basites	372	34,211	0.190 ± 0.013	0.084 ± 0.006	0.141 ± 0.008	0.020 ± 0.002	0.053 ± 0.004	0.017 ± 0.001
Mesites	192	6745	0.220 ± 0.017	0.097 ± 0.008	0.277 ± 0.017	0.043 ± 0.003	0.080 ± 0.008	0.035 ± 0.003
Acidites	644	30,001	0.080 ± 0.005	0.035 ± 0.002	0.269 ± 0.011	0.052 ± 0.003	0.073 ± 0.004	0.028 ± 0.001
Alcaly hyperbasites	146	1635	0.535 ± 0.062	0.235 ± 0.027	0.164 ± 0.016	0.041 ± 0.006	0.079 ± 0.011	0.041 ± 0.005
Alcaly basites	3012	3326	0.450 ± 0.031	0.198 ± 0.014	0.250 ± 0.019	0.067 ± 0.005	0.101 ± 0.008	0.045 ± 0.003
Alcaly mesites	163	5933	0.220 ± 0.023	0.097 ± 0.010	0.303 ± 0.024	0.076 ± 0.005	0.079 ± 0.008	0.042 ± 0.003
Alcaly acidites	79	1082	0.060 ± 0.012	0.026 ± 0.005	0.255 ± 0.059	0.085 ± 0.016	0.041 ± 0.008	0.023 ± 0.003

n—number of samples, N—total number of analyses.

In addition to the previously noted connection with titanium [1], the phosphorus content in hyperbasites can positively correlate with aluminum and ferrous oxide, and even negatively (in picrites) with alkalis, and the values of the PCaM module in picrites are positively correlated with magnesium. Both of the latter correlations are very peculiar.

3.2. Basites

The geochemistry of phosphorus in basites, *i.e.* igneous rocks containing SiO₂ from 45% to 53%, is in many respects similar to that in hyperbasites, due to the close genetic relationship of both.

As can be seen in **Table 1**, the average median (with approximately a two-sigma deviation of the median) values of basite phosphateness calculated on the basis of 372 samples are 0.190 ± 0.013 for P₂O₅, PTiM, PCaM, PFeM and PFe(t)M, respectively (or 0.084 ± 0.006 for elementary P), 0.141 ± 0.008, 0.020 ± 0.002, 0.053 ± 0.004 and 0.017 ± 0.001. *These figures can be considered our Clarke estimates for the basites.* Thus, the near-Clarke P₂O₅ contents in normal (non-alkaline) basites fall within the range of 0.18% - 0.21%.

In addition to the most common phosphorus-titanium bond, the phosphorus content (or the values of phosphorus modules) in basites, as a rule, are positively correlated with alkalis (especially potassium!), even more sharply with the apacity module (NaCaM)³, and less often with iron oxide. As for negative correlations, they are most often manifested with calcium or magnesium, or with both of these elements, and sometimes with aluminum.

3.3. Mesites

Mesites, *i.e.* igneous rocks of medium composition (SiO₂ = 54% - 64%) occupy an intermediate position between basites (SiO₂ = 45% - 53%) and acidites (SiO₂ = 65% - 78%), being closely related to one or the other. For this reason, mesites often do not have clear boundaries, so that some (small) part of the mesite sam-
³Apacity module (NaCaM) = (Na₂O + CaO)/Al₂O₃

ples turns out to be among basites or acidites. Due to the “intermediate”, non-independent position of mesites in the petrogenetic series of igneous rocks, they are often present in close association with either basites (rocks more phosphorous) or acidites (rocks less phosphorous).

As shown in **Table 1**, the average median ($Me \pm 2\sigma_{Me}$) values for mesites obtained on the basis of 192 samples are $0.220\% \pm 0.017\%$ for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively (or $0.097\% \pm 0.008\%$ for elementary P), 0.278 ± 0.017 , 0.043 ± 0.003 , 0.080 ± 0.008 and 0.035 ± 0.003 . These figures can be considered our estimates of clarks for mesites, and the “near-clark” contents of P_2O_5 in normal (non-alkaline) mesites fall within the range of 0.20% - 0.24%.

Phosphorus in mesites is often positively correlated with titanium. Of the other correlations, the positive relationship of phosphorus with potassium (and, apparently, a negative correlation with sodium), as well as a positive correlation with the aluminosilicon module AM, deserves attention.

3.4. Acidites

Acidites include acidic igneous rocks containing 65% - 78% SiO_2 . According to R. Daly (1936), there is more phosphorus in granites than in acid effusions: 0.073 and 0.040%, respectively. A. A. Beus (1981) has lower Clarke and the difference in figures for granites and rhyolites is slightly smaller: accordingly, 0.06 and 0.05% of the P. A.P. Vinogradov (1962) has a figure of $7 \times 10^{-2}\%$ for granites and granodiorites, *i.e.* the same as that of R. Daly for granites. Finally, according to the summary of V.V. Ivanov (1994), L.N. Ovchinnikov has a Clarke of granodiorites—0.098% P, and granites—0.060%, A.A. Yaroshevsky has a Clarke of “acid rocks”—0.087% P, *i.e.* something in between for granites and granodiorites. Regarding all these figures, it should be noted that granodiorites really always contain more phosphorus than granites, so combining both will give Clarke a higher rating. In addition, none of our predecessors gave Clarke P estimates for alkaline varieties of acidic rocks.

As can be seen in **Table 1**, the estimates of Clarke values obtained on a huge analytical base for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively, are $0.080\% \pm 0.005\%$ (or $0.035\% \pm 0.002\%$ for elementary P), 0.269 ± 0.011 , 0.052 ± 0.003 , 0.073 ± 0.004 and 0.028 ± 0.001 . *These figures can be considered our Clarke estimates for acidites*, and the “near-Clarke” P_2O_5 contents in normal (non-alkaline) acidites fall within the range of 0.07% - 0.09%.

As a rule, vein granitoids and pegmatoid granitoids turn out to be more phosphorous. Many acidites are characterized by a positive correlation of phosphorus with titanium, and for a number of them—also with aluminum, iron, and less often with calcium or magnesium. The connections with alkalis are changeable and can be both positive and negative. The positive relationship of phosphorus with aluminum leads to a “induced” negative correlation of phosphorus with silicon, respectively, but to a positive correlation of phosphorus with the aluminosilicon modulus AM and to a negative correlation with the apacity of acidites, *i.e.* with the value of $NaCaM = (Na_2O + K_2O)/Al_2O_3$.

3.5. Alkalites (Alkaline Magmatites)⁴

The most striking feature of the magmatic geochemistry of phosphorus is the accumulation of P in alkaline gabbroids, which has a fairly reliable physico-chemical explanation ([11], p. 14-18). This phenomenon is explained by the low fugitivity of volatile, low polymerization of silicon-oxygen radicals, high probability of formation of sybotactic groups and AlPO_4 complexes, high content of strong cations ($\text{Me}^{3+}\text{PO}_4$ complex) and alkaline-carbonate composition of the deep fluid phase (CO removes PO_4^{3-} from metals). According to the summary of O.B. Dudkin, the average P content in the early facies of calcite carbonatites is 1.4%, and the appearance of apatite-nepheline rocks of the Khibiny type is explained by a slight shift of the initial nepheline melts to the region of phonolites ([11], p. 14–18).

Consideration of the data on the geochemistry of phosphorus in alkalites (alkaline magmatites) for four traditional groups distinguished by silicic acid—hyperbasite, basite, mesite and acidite allows their comparison with the corresponding Clarkes for normal (non-alkaline) alkalites (Table 2).

This comparison shows that alkaline hyperbasites are more than four times enriched in phosphorus, and alkaline basites are more than twice. Mesites do not differ from their alkaline analogues in phosphorus content, and normal acidites are even richer than their alkaline analogues by approximately 25% (P_2O_5 Clarkes $0.080\% \pm 0.005\%$ and $0.060\% \pm 0.012\%$, respectively).

At the same time, the comparative values of phosphoricity indicators in normal and alkaline magmatites partly coincide, and partly do not:

- the content of P_2O_5 in normal magmatites is maximal in mesites, and in alkaline—in hyperbasites; the values of PFeM and PFe(t)M in normal magmatites are maximal in mesites, and in alkaline—in basites; the modules of PTiM and PCaM are maximal in acidites in both groups.

Table 2. Comparison of Clarke phosphoricity indices for magmatites of different alkalinity.

Magmatites	Normal					Alkaline				
	P_2O_5 , %	PTiM	PCaM	PFeM	PFe(t)M	P_2O_5 , %	PTiM	PCaM	PFeM	PFe(t)M
Hyperb-asites	0.123 ± 0.031	0.197 ± 0.031	0.022 ± 0.003	0.026 ± 0.008	0.009 ± 0.003	0.535 ± 0.062	0.064 ± 0.0016	0.041 ± 0.006	0.079 ± 0.011	0.041 ± 0.005
	0.190 ± 0.013	0.141 ± 0.008	0.020 ± 0.002	0.053 ± 0.004	0.017 ± 0.001	0.450 ± 0.031	0.250 ± 0.019	0.067 ± 0.005	0.101 ± 0.008	0.045 ± 0.003
Mesites	0.220 ± 0.017	0.278 ± 0.017	0.043 ± 0.003	0.080 ± 0.008	0.035 ± 0.003	0.220 ± 0.023	0.303 ± 0.024	0.076 ± 0.005	0.079 ± 0.008	0.042 ± 0.003
	0.080 ± 0.005	0.269 ± 0.011	0.052 ± 0.003	0.073 ± 0.004	0.028 ± 0.001	0.060 ± 0.012	0.255 ± 0.059	0.085 ± 0.016	0.041 ± 0.008	0.023 ± 0.003

⁴We draw readers' attention to the fact that the term *alkalites* is not used here quite "legitimately"—solely for brevity. The fact is that this term was pre-occupied in our book, where rocks with a sum of alkalis $\geq 8\%$ were so called ([28], pp. 243-252). Here (*i.e.* in petrochemistry—for igneous rocks), the boundary of "alkalites" varies depending on the silicic acid content of the rock.

Regarding the revealed correlations of phosphoricity indicators, the following can be noted.

In alkaline hyperbasites, phosphorus bonds with titanium are most often fixed, and less often with alkalis, calcium and manganese. Various correlations of phosphorus modules are noted here, for example, PCaM (*i.e.* apatite phosphorus) with iron and potassium, PFeM with aluminum, as well as not quite clear negative (!) correlations of the PCaM module with aluminum and even (in some nephelinites) with fluorine.

In alkaline basites, it is also most often noted the bonds of phosphorus and a number of phosphorus modules with titanium and iron, as well as potassium (and with sodium, on the contrary, the correlation is negative), sometimes with manganese. A negative correlation of phosphorus with magnesium is also characteristic (which was also found in alkaline hyperbasites).

In alkaline mesites, in addition to the usual connection with titanium, positive correlations of phosphorus with magnesium are quite common, which distinguishes these rocks, since in more basic rocks the correlation with magnesium is usually negative.

In alkaline acidites, in addition to the usual phosphorus-titanium bond, correlations with calcium, potassium and general femicity are noted.

4. Hydrothermalites

Some geochemical features of phosphorites and phosphate-containing rocks quite definitely point to the hydrothermal process as a source of phosphorus. Most often phosphorus-containing hydrotherms are volcanogenic, but sometimes the direct connection of hydrotherms with volcanism is not visible, as N.G. Brodskaya clearly wrote ([9], p. 10). In the metalliferous sediments of the East Pacific Uplift, phosphorus positively correlates with hydrothermal iron, which shows the most likely mechanism of phosphorus entering the sediment—co-deposition with $\text{Fe}(\text{OH})_3$ [29].

As can be seen in **Table 3**, the estimates of Clarke values in hydrothermalites obtained on a fairly large analytical base for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively, are $0.130\% \pm 0.017\%$ (or $0.057\% \pm 0.007\%$ for elementary P), 1.054 ± 0.210 , 0.055 ± 0.016 and 0.014 ± 0.003 .

In most hydrothermalites, most often there is a positive correlation of phosphorus with iron, caused by the fact that iron and manganese hydroxides are carriers of phosphorus. Sometimes there was also a correlation of phosphaticity with alkalis or with the carbonate content of hydrothermalites. In siliceous hydrothermalites (jasperites, jaspers) silica is a diluent for phosphorus, which causes the appearance of a negative correlation of P_2O_5 and SiO_2 . In manganese hydrothermal ores, the nature of correlations of phosphorus or phosphorus modules suggests the presence of not one, but at least two phosphorus carriers—hydroxide and clay.

Table 3. Phosphorus content and values of phosphorus modules for hydrothermalites and metamorphites.

Rocks	n	N	P ₂ O ₅ , %	P, %	PTiM	PCaM	PFeM	PFe(t)M
Hydrothermalites	255	1692	0.130 ± 0.017	0.057 ± 0.007	1.054 ± 0.210	0.055 ± 0.016	0.014 ± 0.003	0.012 ± 0.002
Ores-hydrothermalites	59	184	0.220 ± 0.070	0.097 ± 0.031	1.969 ± 0.649	0.061 ± 0.031	0.031 ± 0.021	0.017 ± 0.008
Meta-basites and meta-hyperbasites	328	3436	0.190 ± 0.014	0.084 ± 0.006	0.139 ± 0.008	0.022 ± 0.002	0.050 ± 0.003	0.015 ± 0.001
Meta-mesites	73	543	0.160 ± 0.028	0.070 ± 0.012	0.195 ± 0.030	0.042 ± 0.007	0.064 ± 0.012	0.021 ± 0.004
Meta-acidites	145	1611	0.100 ± 0.012	0.044 ± 0.005	0.216 ± 0.025	0.064 ± 0.015	0.050 ± 0.010	0.022 ± 0.002
Meta-psammites	300	3498	0.090 ± 0.009	0.040 ± 0.004	0.204 ± 0.013	0.061 ± 0.008	0.054 ± 0.007	0.023 ± 0.002
Meta-pelites	184	11084	0.120 ± 0.012	0.053 ± 0.005	0.145 ± 0.013	0.089 ± 0.012	0.045 ± 0.006	0.016 ± 0.002
Meta-silicites	73	515	0.130 ± 0.042	0.057 ± 0.019	1.184 ± 0.381	0.163 ± 0.057	0.015 ± 0.009	0.010 ± 0.004
Apo-weathering crusts metamorphites	111	556	0.120 ± 0.019	0.053 ± 0.008	0.130 ± 0.015	0.138 ± 0.040	0.038 ± 0.007	0.015 ± 0.003
Meta-carbonates	66	314	0.065 ± 0.017	0.029 ± 0.008	0.455 ± 0.101	0.002 ± 0.001	0.099 ± 0.026	0.036 ± 0.008
Allochemical metamorphites	239	1452	0.160 ± 0.018	0.070 ± 0.008	0.187 ± 0.017	0.073 ± 0.013	0.056 ± 0.009	0.025 ± 0.003

5. Metamorphites

According to R.M. Fayzullin's generalization ([30], p. 21), in the facies of green shales (*i.e.* at temperatures of 200°C - 450°C) and amphibolite (450°C - 650°C) phosphorus is mostly inert or weakly mobile. Apatite mineralization can appear only with selective dissolution and recrystallization of the initial phosphate-containing rocks. These are the metamorphic deposits of apatite in the Southern Baikal region, the Erzinsky and Bochorinsky ore occurrences.

Since there are manifestations and deposits of apatite in the Archean metamorphites of the Aldan shield, a natural question arose: is phosphorus not controlled by the processes of metamorphism and migmatization? This could be judged by determining the phosphorus content in minerals. It turned out ([31], p. 65), that the presence of a certain amount of phosphorus in minerals of various genetic types of migmatites, the absence of phosphorus enrichment of minerals and rocks of lower-temperature facies, low phosphorus content in granites of the early Precambrian—all this confirms the conclusion that during the processes of metamorphism and migmatite formation, there are no significant movements of this element.

The statistical estimates obtained by us for metamorphites were summarized in **Table 3**. They allow comparison of Clarke indicators for metamorphites and their primary substrate—protolith (**Table 4**)⁵.

⁵Clarke estimates for sedimentary rocks are given in **Table 5**.

Table 4. Comparison of Clarke phosphoricity indices for protoliths and corresponding metamorphites.

Rocks	Non-metamorphosed rocks					Metamorphites				
	P ₂ O ₅ , %	PTiM	PCaM	PFeM	PFe(t)M	P ₂ O ₅ , %	PTiM	PCaM	PFeM	PFe(t)M
Hyperbasites	0.123 ± 0.031	0.197 ± 0.031	0.022 ± 0.003	0.026 ± 0.008	0.009 ± 0.003	0.190 ± 0.013	0.141 ± 0.008	.020 ± 0.002	0.053 ± 0.004	0.017 ± 0.001
	Basites	0.141 ± 0.008	0.020 ± 0.002	0.053 ± 0.004	0.017 ± 0.001					
Mesites	0.220 ± 0.017	0.278 ± 0.017	0.043 ± 0.003	0.080 ± 0.008	0.035 ± 0.003	0.160 ± 0.028	0.195 ± 0.030	0.042 ± 0.007	0.064 ± 0.012	0.021 ± 0.004
	Acidites	0.080 ± 0.005	0.269 ± 0.011	0.052 ± 0.003	0.073 ± 0.004	0.028 ± 0.001	0.100 ± 0.012	0.100 ± 0.012	0.216 ± 0.025	0.050 ± 0.010
Psammites	0.110 ± 0.006	0.229 ± 0.011	0.066 ± 0.008	0.055 ± 0.005	0.028 ± 0.001	0.090 ± 0.009	0.204 ± 0.013	0.061 ± 0.008	0.054 ± 0.007	0.023 ± 0.002
	Pelites	0.140 ± 0.005	0.168 ± 0.008	0.116 ± 0.011	0.039 ± 0.003	0.021 ± 0.001	0.120 ± 0.012	0.145 ± 0.013	0.089 ± 0.012	0.045 ± 0.006
Carbonates	0.050 ± 0.008	0.438 ± 0.057	0.0014 ± 0.0003	0.067 ± 0.008	0.034 ± 0.004	0.065 ± 0.017	0.455 ± 0.121	0.002 ± 0.001	0.099 ± 0.026	0.036 ± 0.008
	Silicites	0.080 ± 0.006	0.267 ± 0.037	0.089 ± 0.017	0.049 ± 0.006	0.021 ± 0.002	0.130 ± 0.042	1.184 ± 0.381	0.163 ± 0.057	0.015 ± 0.009
Weathering crusts	0.150 ± 0.016	0.127 ± 0.052	0.160 ± 0.042	0.018 ± 0.004	0.013 ± 0.003	0.120 ± 0.019	0.130 ± 0.015	0.138 ± 0.040	0.038 ± 0.007	0.015 ± 0.003

Table 5. Phosphorus content and values of phosphorus modules for rocks of the biosphere and sedimentary shell.

Rocks	n	N	P ₂ O ₅ , %	P, %	PTiM	PCaM	PFeM	PFe(t)M
Soils	52	260	0.090 ± 0.017	0.040 ± 0.008	0.188 ± 0.025	0.082 ± 0.018	0.030 ± 0.006	
Paleosoils	23	83	0.070 ± 0.034	0.031 ± 0.015	0.085 ± 0.057	0.002 ± 0.001	0.011 ± 0.007	0.010 ± 0.004
Sediments	82	643	0.160 ± 0.019	0.070 ± 0.008	0.320 ± 0.042	0.038 ± 0.005	0.038 ± 0.005	0.031 ± 0.003
Psammites	529	29,583	0.110 ± 0.006	0.048 ± 0.003	0.229 ± 0.011	0.066 ± 0.008	0.055 ± 0.005	0.028 ± 0.001
Pelites	632	32,131	0.140 ± 0.005	0.062 ± 0.002	0.168 ± 0.008	0.116 ± 0.011	0.039 ± 0.003	0.021 ± 0.001
Carbonates	209	6750	0.050 ± 0.008	0.022 ± 0.003	0.438 ± 0.057	0.0014 ± 0.0003	0.067 ± 0.008	0.034 ± 0.004
Silicites	236	5336	0.080 ± 0.006	0.035 ± 0.003	0.267 ± 0.037	0.089 ± 0.017	0.049 ± 0.006	0.021 ± 0.002
Weathering crusts	93	362	0.120 ± 0.021	0.053 ± 0.009	0.094 ± 0.019	0.133 ± 0.034	0.019 ± 0.003	0.015 ± 0.002
Bauxite	22	130	0.155 ± 0.037	0.068 ± 0.016	0.066 ± 0.015	0.534 ± 0.241	0.014 ± 0.004	0.010 ± 0.003
Weathering crust ores	65	1296	0.132 ± 0.029	0.058 ± 0.0123	0.333 ± 0.229	0.123 ± 0.057	0.008 ± 0.004	0.007 ± 0.003
All: weathering crust and their ores	205	1860	0.150 ± 0.016	0.066 ± 0.007	0.127 ± 0.052	0.160 ± 0.042	0.018 ± 0.004	0.013 ± 0.003
Nodules	48	222						
Rare lithotypes	29	150	0.080 ± 0.019	0.035 ± 0.008				

Note. n is the number of samples, N is the total number of analyses.

Such a comparison shows that the following ratios are observed *in the group of metamorphites on the substrate of igneous rocks*:

1) Average median values of phosphoricity for a set of *meta-basites* (together with *meta-hyperbasites*) were obtained on the basis of 328 samples covering 3436 analyses. The estimates for basites and meta-basites turned out to be almost the same, moreover, such a comparison is complicated by the fact that we are forced not to separate meta-basites from meta-giperbasites, because they are often connected by gradual transitions. This means that, in general, the processes of isochemical metamorphism of large magmatic complexes do not really lead to a change in the phosphorus content in the protolith.

2) As in non-metamorphosed basites, the most typical for meta-basites are positive phosphorus bonds (or phosphorus modules) with titanium and iron, and negative ones with magnesium.

3) Nevertheless, the diversity of phosphorus correlations found in some samples of meta-basites (including such unusual ones as negative associations with alkalis or with calcium) seems to reflect the influence of allochemical processes in which phosphorus could exhibit local mobility.

4) Average median values of phosphoricity for a set of *meta-mesites* were obtained on the basis of 73 samples covering 543 analyses. The apparent heterogeneity of the studied analytical sets also explains the absence of significant correlations of phosphorus (or phosphorus modules) with other indicators of the composition of metamesites. In general, phosphorus meta-mesites ($P_2O_5 = 0.160\%$ vs. 0.220%), PTiM modules (0.195 vs. 0.278) and PFeM (0.064 vs. 0.080) are noticeably poorer than their non-metamorphosed analogues, which indicates a possible phosphorus removal during metamorphism.

5) Average median values of phosphoricity for a set of *meta-acidites* were obtained on the basis of 145 samples covering more than 1600 analyses. Meta-acidites are inferior to their possible protolith in three modules, but the picture is just the opposite for phosphorus and the PCaM module. It is difficult to understand this, but it would be too risky to talk about the introduction or removal of phosphorus during metamorphism.

In the group of metamorphites on the substrate of sedimentary rocks, as can be seen in **Table 3** and **Table 4**, the ratios are as follows:

6) Average median values of phosphoricity for a set of *meta-psammites* were obtained on the basis of 300 samples covering about 3500 analyses. The estimates for phosphorus and most modules in meta-psammites are lower than in their non-metamorphosed counterparts, which may indicate phosphorus removal during metamorphism. Correlations in meta-psammites are generally the same as in their protolith.

7) Average median values of phosphoricity for a set of *meta-pelites* were obtained on the basis of 184 samples covering more than 11 thousand analyses. The observed ratios of phosphorus and phosphorus modules are approximately the same as in the group of metapsammites.

8) Average median values of phosphoricity for a set of *meta-silicites* were obtained on the basis of 184 samples covering more than 11 thousand analyses. Silicites turned out to be much poorer in phosphorus compared to meta-silicites. However, metamorphism is hardly the reason for this difference. Most likely, the primary chemogenic sediments of Precambrian chemogenic meta-silicites were initially richer in phosphorus than biogenic sediments of Phanerozoic silicites (radiolarites, spongolites, diatomites).

9) Average median values of phosphoricity for a set of *apoweathering crusts metamorphites* were obtained on the basis of 111 samples covering more than 550 analyses. These formations (metamorphosed former weathering crusts) is noticeably poorer in phosphorus than their supposed protolith ($P_2O_5 = 0.12\%$ vs. 0.15%). Also, their phosphorus-calcium modulus is lower ($PCaM = 0.138$ vs. 0.160). Nevertheless, the phosphorus-hydroxide modulus in meta-hydrolysates is noticeably higher ($PFeM = 0.038$ vs. 0.018), which reflects the dominance of hydroxide-sorbed phosphorus in meta-hydrolysates. However, due to the great uncertainty in the diagnosis of protolith, our comparisons are not very reliable.

10) Average median values of phosphoricity for a set of ancient meta-carbonate rocks were obtained on the basis of 66 samples covering more than 300 analyses. Meta-carbonates, on the contrary, are somewhat richer in phosphorus than non-metamorphosed carbonates. The reason, apparently, should not be sought in metamorphism, since almost all marbles and calcifyres are Precambrian formations, even Archean. It is quite possible that the primary carbonate sediments of this age were formed in basins whose waters were richer in phosphorus than in the Phanerozoic.

6. Allochemical Metamorphites

As noted in the “Geochemistry of Titanium” ([1], p. 181), in contrast to the predominantly isochemical regional metamorphism, where titanium usually behaves inert, with allochemical metamorphism, especially with the introduction of alkalis, titanium can exhibit significant mobility. Since phosphorus is often correlated with titanium, this conclusion is also true for it. Moreover, due to the volatility of some phosphorus compounds, high-temperature magmatic, but especially post-magmatic and metamorphic hydrothermal processes can be accompanied by phosphoric metasomatism. So, in his summary V.E. McKelvey notes the introduction of phosphorus in the processes of alkaline metasomatism ([22], p. 35):

“Although phosphorus, which is part of the rock, is not very strongly affected by metamorphic processes, it is usually introduced during alkaline metasomatism, including albitization and kalishpatization when exposed to hydrothermal solutions <...>, and also, the phenitization associated with carbonatite complexes <...>. The phosphate content in rocks subjected to such metasomatism may increase to 0.4% - 0.6%.”

Judging by R.M. Fayzullin's summary ([30], p. 22-23), phlogopite deposits are associated with the formation of calcareous-magnesian metasomatites. As for alkaline metasomatites, complex deposits of iron, uranium and rare earths, formed in stages and also containing phosphorus, are associated with them. The vertical zonality of the distribution of ore components, including phosphorus, is clearly manifested in alkaline metasomatites ([30], p. 24).

On the Aldan shield, apatite occurrences of magnesian skarns and apatite-kalishpat metasomatites are common within the Ungrino-Timpton synclinorium. There are developed rocks of the gabbro-plagiogranite formation and spatially associated with them apatite-containing magnesian rocks, which are associated with well-known iron ore deposits—Taiga, Pioneer, Des, etc. According to A.R. Entin and Yu.V. Kiselev ([32], p. 143), these skarns and metasomatites show a distinct geochemical relationship with the main rocks of the gabbro-plagiogranite formation. The background content of P_2O_5 in iron ore rocks is 0.1% - 0.2%. A.R. Entin and Yu.V. Kiselev reject the idea of borrowing phosphorus from host marbles and calcifyres (in which there is very little phosphorus) and adhere to the idea of a deep introduction of phosphorus in metasomatism.

In Northern Kazakhstan, small-depth metasomatic manifestations of apatite are known, located in secant structures among sedimentary, volcanogenic-sedimentary and even igneous rocks. The most characteristic the first are in the Karadok limestones, with clear near-ore changes represented by newly formed calcite, dolomite, ankerite, as well as albite, chlorite, quartz, sericite, kaolinite, hematite and fluorite. According to I.G. Chentsov [33], phosphorus was transferred in carbon dioxide alkaline solutions.

Nevertheless, unlike titanium, for which high-temperature metasomatic processes associated with hydrotherms and contact metamorphism were of primary importance ([1], p. 181-188), *the phenomena of metasomatism accompanying hypergenic processes are most important in phosphorus geochemistry*. Typical examples of metasomatic phosphorites, even of industrial importance, are the so-called “white phosphorites” on the heads of Upper Silurian limestones in state Tennessee and phosphatized limestones of the Lower Eocene in state Florida.

Judging by the data shown in **Table 3**, in a very heterogeneous set of compositions of metasomatites (allochemical metamorphites) according to 239 samples covering more than 1450 analyses, the median values (approximately with a two-sigma deviation of the median) for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively, are $0.160\% \pm 0.018\%$ (or $0.070\% \pm 0.008\%$ for elementary P), 0.187 ± 0.017 , 0.073 ± 0.013 , 0.056 ± 0.009 and 0.025 ± 0.003 . It is obvious that phosphorus can be introduced in the processes of metasomatism (the conditions of which are not fully understood). At least with the largest averaging, about 20% of all studied samples of metasomatites show a clear accumulation of phosphorus.

The analytical samples show the usual correlations for phosphorus with tita-

niium and iron, as well as with alkalis, aluminum and calcium. Sometimes unusual correlations are also detected, such as a positive correlation with silicon or a negative correlation with the hydrolysate module of GM [28]. This can be considered the specificity of metasomatites, which distinguishes them from other rocks, including isochemical metamorphites.

7. Biosphere

Following the heading we used earlier [1] [2], this chapter contains materials on the geochemistry of phosphorus in two biospheric objects: soils and sediments.

7.1. Soils

We managed to collect not very many complete analyses of modern soils. There are even fewer analyses of fossil soils (paleosoils), especially of such ancient ones as the Pre-Rifaeen ones.

As can be seen in **Table 5**, for 52 samples of modern soils covering 261 analyses, the median values (with approximately a two-sigma deviation of the median) for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively, are $0.090\% \pm 0.017\%$ (or $0.040\% \pm 0.008\%$ for elementary P), 0.188 ± 0.025 , 0.082 ± 0.018 and 0.030 ± 0.006 .

Despite the fact that the main supplier of phosphorus in soils is undoubtedly soil organic matter (humus), we have not found any significant correlations of phosphorus or phosphorus modules with C_{org} (or with a roughly equivalent value of LDC—losses during calcination). This means that the primary form of organic phosphorus P_{org} is rapidly transformed in the soil and passes into various types of mineral phosphorus— P_{min} .

Most often, a correlation of phosphorus with alkalis is detected, which most likely means that the phosphate content is related to the clay content of the soil, less often it is possible to fix the connection of phosphorus with titanium or magnesium. The positive correlation of phosphorus with sodium noted several times is curious. It may mean that phosphorus forms some kind of compound with sodium in the soil profile, for example, soluble sodium dihydrogen phosphate $NaH_2(PO)_4$. Some correlations are peculiar. This is an unusual negative correlation of phosphorus with a possible mineral carrier of phosphorus (often noted in hypergenesis)—iron oxide Fe_2O_3 or with common iron $Fe_2O_3 + FeO$. The meaning of such antagonism is poorly understood.

Fossil soils (paleosoils) are generally poorer in phosphorus compared to modern soils, which may indicate partial removal of phosphorus during burial and further lithification of ancient soils. However, it seems that the correlations of phosphorus or phosphorus modules in paleosol.

It remains approximately the same as in modern soils.

7.2. Sediments

We can separately consider alluvial sediments (for which we have little data),

lake and marine (oceanic). It is known that biogenic phosphorus— P_{bio} predominates in sediments, having two main forms—phosphorus of organic matter P_{org} and phosphorus of skeletal remains— P_{min} . In relatively shallow shelf and hemipelagic sediments accumulated at a high rate, the balance of total phosphorus is dominated by P_{org} , and in pelagic sediments deposited at a low rate—biogenic P_{min} .

With the process of diagenesis and decomposition of organic matter (OM), the former P_{org} leaves the sediment and partly returns to the bottom water, and partly is fixed on the iron, calcium or titanium barriers in the form of the mineral phosphorus P_{min} . *But in general, the removal of phosphorus in the process of lithification of sediment leads to the fact that sedimentary rocks are poorer in phosphorus than the original sediments.*

The most phosphorus-rich terrigenous marine and ocean sediments, and among them—the most clay. Siliceous sediments are generally poorer than terrigenous ones, and pure carbonate sediments are the poorest in phosphorus. According to G.N. Baturin, the exception to this general pattern is the zones of shelf upwelling with abnormal phosphorus contents in diatom silts and with the rudimentary formation of nodular phosphorites. A special place among the sediments is occupied by alluvial enriched with iron and manganese; they are often show abnormally high phosphaticity due to the sorption of phosphorus on iron hydroxides.

The most characteristic for a number of sediments is the negative correlation of the phosphorus-iron module PFeM with magnesium, which does not have a clear interpretation. Other correlations (for example, the positive relationship of phosphorus with alkalis or with titanium with simultaneous antagonism of phosphorus with silicon) are quite understandable—they are explained by the attraction of phosphorus to the clay component of the sediments.

8. The Stratisphere

The *stratisphere* is understood as the shell of the Earth, composed of sedimentary rocks⁶.

In this chapter, the distribution of the content of P_2O_5 and phosphorus modules is considered both in the main types of sedimentary rocks (terrigenous, carbonate and siliceous) and in rarer, but important minerals (for example, in alumina). To complete the coverage of the topic, the long-published essays on the geochemistry of phosphorus in carbonaceous biolites—coal and black shale are summarized here [34] [35] [36]. In addition, volcanogenic sedimentary rocks are an important component of the stratisphere, in the genesis of which endogenous processes (formation of the source material) are closely intertwined with the exogenous mechanism of sedimentation. The term *tuffoids* is used for such rocks [28].

⁶Note that there is no term “*stratisphere*” in Western geology; its full semantic analogue is the English-language term “*sedimentary shell*”.

8.1. Psammites

As before ([2]; 1, p. 232), *psammites* are understood as clastic sedimentary rocks, both loose (gravels, sands, siltstones) and lithified (gravelites, sandstones, siltstones). The diversity of psammites is determined by the diversity of their mineral composition: both the terrigenous detrital part (quartz and feldspar with a small admixture of other minerals), and especially the variability of their autigenic cement—clay or carbonate, and sometimes even siliceous. This diversity determines the varieties of psammites, which is expressed in their chemical composition by variations in the contents of rock-forming SiO_2 , Al_2O_3 , K_2O , Na_2O and CO_2 . The content of the small component P_2O_5 is usually correlated with such variations in one way or another. The most reliable indicator, which had the “last word” in attributing the terrigenous mixed rock to the psammite group, was the hydrolysate module (GM)⁷. Only substantially arkose sandstones can have a GM value of more than 0.30 and be certified as *siallites*, whereas the vast majority of psammites have a GM value of <0.30 , *i.e.* are certified as *silites*.

As already noted ([1], p. 234), the combining by A.B. Ronov siltstones with sandstones into “Aleuro-sandstones rocks” does not deserve the harsh criticism to which it was subjected by academician N.M. Strakhov. Such combining is quite correct for humic deposits, in which the chemical composition of siltstones is closer to sands than to clays. However, in the strata of arid (usually red-colored) siltstones, in their chemistry, are closer to clays than to sands, so the association “siltstone-clay rocks” is correct here [28].

As can be seen in **Table 5**, the average median ($\text{Me} \pm 2\sigma_{\text{Me}}$) values for the totality of all psammites studied by us, obtained on the basis of 529 samples, are $0.110\% \pm 0.006\%$ for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively (or $0.048\% \pm 0.003\%$ for elementary P), 0.229 ± 0.011 , 0.066 ± 0.008 , 0.055 ± 0.005 and 0.028 ± 0.001 . *These figures can be considered as our estimates of Clarkes for psammites.*

In psammites with Clarke or lower-Clarke contents of P_2O_5 , the main carrier of phosphorus is a clay substance, as evidenced by at least three empirical patterns. Firstly, siltstones, as a rule, are richer in phosphorus than sandstones; secondly, negative correlations of P_2O_5 with SiO_2 and even Na_2O are often manifested in psammites, indicating that the detrital components of psammites (quartz and plagioclase) are diluents of phosphorus concentrations. Thirdly, in addition to the usual correlation of phosphorus with titanium, the positive correlation of P_2O_5 with MgO is very characteristic of psammites, indicating the entry of phosphorus into clay minerals (smectite or chlorite), as well as the often manifested positive correlation of phosphorus with the hydrolysate module (GM).

However, high-phosphate sandstones with a minimal proportion of clay matter sometimes turn out to be just high-silica quartz sandstones! This paradoxical

⁷See our book: *Yudovich Ya. E., Ketris M. P. Fundamentals of Litochemistry—Tyumen: International Publishing House “World Sci. Publ”, 2022. 484 pp.*

empirical regularity is connected with the nature of such sandstones as the products of erosion and redeposition of former weathering crusts, many of which are characterized by the accumulation of phosphorus. Perhaps the most striking manifestation of this pattern is the accumulation of phosphorus in the basal thickness of the Ordovician of the Northern Urals ([37], p. 55).

The often observed positive correlation of phosphorus with oxide iron (or even with total iron) in psammites reflects a characteristic property of the hypergenic geochemistry of phosphorus—the sorption of phosphate on iron hydroxides.

The characteristic correlations of phosphorus (or phosphorus modules) with iron and titanium do not necessarily have to be interpreted in terms of geochemical barriers (iron or titanium). In psammites, such a correlation can be created simply due to the natural dressing of sandy or siltstone sediment, when the heavy fraction includes accessories—both iron- and titanium-containing (for example, ilmenite and leucoxene) and phosphate-containing (apatite); therefore, the simultaneous increase in the content of titanium, iron and phosphorus in the rock, which creates a correlation, can occur simply as the yield of the heavy fraction increases.

The ratio of phosphorus in psammites with carbonate admixture has a dual character: in some cases there is a negative correlation of P_2O_5 and CO_2 , in others, on the contrary, the correlation is positive—more carbonate psammites turn out to be more phosphate. It can be assumed that this empirical pattern is related to the climate: humid for the former or arid for the latter, since phosphorus accumulation is characteristic of arid precipitation.

8.2. Pelites

Pelites are clay sedimentary rocks, both loose (clays) and lithified in catagenesis, called *mudstones* and *clay shales*.

A large material diversity of pelites is determined by the close connection of the clay substance prevailing in them (composed of kaolinite, smectite, hydro-mica and chlorite) with detrital, siliceous and carbonate impurities. The former are created by the siltstone component, so that such rocks are connected by a continuous transition with siltstones and are usually called siltstone. The admixture of biogenic silica in clay rocks generates an extensive group of siliceous-clay rocks, which also do not have a clear boundary with the clay ones themselves. Finally, carbonate impurities give rise to a whole series of mixed carbonate-clay rocks, which have long received the special name “marls”, although in fact many marls can also be carbonate-psammite, and not only carbonate-clay [38]. In general, mixed rocks containing no more than 65% - 67% SiO_2 and no less than 15% Al_2O_3 , with an indispensable predominance of potassium over sodium (*i.e.* having an alkaline modulus $AlkM = Na_2O/K_2O$ less than 0.5), as well as all “marls” in which the amount of carbonates was less than 50%—were attributed as pelites But the most informative classification in-

indicator, which had the “last word” in referring the terrigenous mixed rocks to the pelite group, was, of course, the hydrolysate modulus >0.30 , which forced the rock to be certified as *siallite*.

Among the major works on the geochemistry of phosphorus in clay rocks, the studies of A.B. Ronov and G.A. Korzina on the average composition of sedimentary strata [39] and S.B. Felitsyn, devoted to ancient clay shales of the East European Platform, should be mentioned ([40], p. 375). Thus, based on the analysis of 544 average clay samples made up of 10130 samples, A.B. Ronov and G.A. Korzina [39] found that the content of P_2O_5 in them ranges from 0.070% (humid, continental and lagoon) to 0.132% (humid, pelagic). Phosphorus is considered biogenic because ([39], p. 685):

“...its stratigraphic distribution runs parallel with the C_{org} . The observed deviations (C_1 , K_1) affect clays of a humic origin, where phosphorus could not crystallize in an acidic environment.”

As follows from **Table 5**, the average median ($Me \pm 2\sigma_{Me}$) values for the totality of all pelites, obtained on the basis of 633 samples, are $0.140\% \pm 0.005\%$ for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively (or $0.062\% \pm 0.002\%$ for elementary P), 0.168 ± 0.008 , 0.116 ± 0.011 , 0.039 ± 0.003 and 0.021 ± 0.001 . *These figures can be considered our estimates of the Clarks for the pelites.*

A significant part of the over-Clarke phosphorus content in pelites is created not by pure, but by mixed clay rocks, in particular, siltstone and carbonate-clay.

In general, the correlations of phosphorus or phosphorus modules in clay rocks turned out to be much more complex than one might have expected. In particular, they are different for ancient and young pelites, and also depend in different ways on the ratio of the clay and clastic component of the pelites, as well as on the overall level of content phosphorus—near-Clarke or over-Clarke. Precambrian clay shales are characterized by correlations indicating the dominance of the accessory apatite form of phosphorus, whereas younger strata (in particular, Mesozoic) are characterized by correlations indicating the presence of sorbed forms of phosphorus—silicate or hydroxide.

The near-Clarke and lower-Clarke phosphorus contents in pelites are characterized by poverty or complete absence of significant correlations of phosphorus with rock-forming components or lithochemical modules. This can be interpreted as an indication of the absence of a dominant form of phosphorus—the comparability of the contribution of its forms: accessory apatite (or francolite), sorbed silicate or sorbed hydroxide. On the contrary, a variety of correlations of phosphorus and/or phosphorus modules is characteristic of pelites with high-grade phosphorus. This means that the accumulation of phosphorus in pelites occurs when one of its forms dominates—accessory mineral or sorbed.

Among the correlations of phosphorus, a positive correlation with magnesium is often manifested, meaning the dominance of its sorbed silicate form on the components of the clay substance—smectite or chlorite. Another common correlation of phosphorus is with iron, meaning the dominance of its sorbed iron-

hydroxide form. As for the carbonate content of pelites, opposite correlations of phosphorus with it were observed—both negative and positive. Thus, in some cases, an admixture of carbonate dilutes the total phosphorus content, and in others, on the contrary, contributes to its concentration.

Cases of unusual correlations of phosphorus, such as negative with titanium, aluminum or a hydrolysate module, and positive with silicon, meaning antagonism of phosphorus with a clay substance, may indicate the dominance of the clastic (accessory apatite) form phosphorus, and in particular cases—a possible admixture in pyroclastics. Another sign of a volcanogenic impurity in the pelites may be the correlation of phosphorus with sodium. The sometimes observed correlation of phosphorus with manganese can probably be explained by the admixture of isomorphic manganese in accessory apatite.

8.3. Carbonate Rocks

Judging by the data in **Table 5**, the average median ($Me \pm 2\sigma_{Me}$) values for the set of all carbonates obtained on the basis of 209 samples are $0.050\% \pm 0.008\%$ for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively (or $0.022\% \pm 0.003\%$ for elementary P), 0.438 ± 0.057 , 0.0014 ± 0.0003 , 0.067 ± 0.008 and 0.034 ± 0.004 . *These figures can be considered our estimates of the Clarkes for carbonate rocks*, which turned out to be twice as low as the Clarkes of their predecessors. Naturally, due to the maximum content of CaO, the phosphorus-calcium modulus (PCaM) is the lowest among sedimentary rocks, and phosphorus-titanium (PTiM) is very high, due to the poor titanicity of most carbonates.

In general, most carbonate rocks are poor in phosphorus; in particular, the phosphorus content in carbonates is three times lower than in pelites (P_2O_5 0.05% vs. 0.14%). This means that despite the experimentally proven ability of freshly deposited carbonates to sorption of phosphate, this process at the Clarke level was limited by a small amount of available phosphate in above-bottom or pore waters.

Since, as is known [39], the main source of Clarke phosphorus of carbonate rocks was biogenic phosphorus of P_{bio} of residual organic matter (OM), the reason for the deficiency of dissolved phosphate during carbonate sedimentation was the deficiency of OM in the carbonate sediment, because most of the initial OM of carbonate fossils decomposed before reaching the bottom of the basin. As a result, pure carbonate sediments turned out to be almost sterile by phosphorus. Only in anoxic environments, in which carbonate sediments with an increased content of C_{org} (future black shales) were formed, phosphorus could be concentrated in high-grade quantities—even in pure carbonate rocks.

However, in most cases, an increase in phosphorus content is observed not in pure, but in mixed carbonate-silicate rocks, in particular, in marls. The study of phosphorus correlations often reveals a positive correlation of P_2O_5 with Al_2O_3 and TiO_2 , and a negative correlation with CaO and especially with MgO. This indicates the concentration of phosphorus in the non-carbonate

components of rocks—usually clay, less often silt, with the diluting role of the carbonate matrix. Only in conditions of avalanche sedimentation (as in orogenic molasses) The OM of carbonate sediments could be protected by clay tires from rapid oxidation, which ensured better preservation of P_{bio} in the carbonate sediment.

Thus, our study allows us to supplement the conclusion of A.B. Ronov [29]: *the main carriers of Clarke phosphorus in carbonate rocks are not only residual organic matter, but, apparently, also silicate-sorbed phosphorus in clay matter.* Less often, it is possible to allow the participation of hydroxide-sorbed phosphorus, although the proportion of such phosphorus is usually also positively correlated with the amount of silicate admixture in the carbonate rock. Sometimes, however, the opposite picture was also observed—a positive correlation of the PFeM module with carbonate content.

8.4. Silicites

As already noted ([1], pp. 300-301), *siliceous rocks* (silicites), which, according to V.T. Frolov, it would be more correct to call *silicic*, are a heterogeneous group. Firstly, Precambrian silicites, when there were no flint organisms in the bio-sphere—formations chemogenic, whereas Phanerozoic—almost all biogenic. Secondly, among Phanerozoic silicites, such biogenic rocks as radiolarites, spongolites and diatomites are very different formations. Thirdly, silicites can be different facially. In any case, in our Ural region, siliceous rocks, as a rule, are deep-water sediments; therefore, they are widely distributed in the paleobathial (“shale”) Lemva zone, and are completely uncharacteristic of the paleoshelf (“carbonate”) Yelets zone. Finally, silicites can also be hydrothermal volcanogenic, a typical example of which is the well-known jasper.

All this generates variability in the chemical composition of silicites, including the phosphorus content in them. Perhaps this is the reason for the lack of reliable estimates of the average compositions of silicites in the literature, because it makes no sense to average the compositions of genetically completely different formations. Note that the biogenic accumulation of phosphorus in diatom silts was known to Georg Berg (1929) ([41], p. 318).

As can be seen in **Table 5**, the average median values (approximately with a two-sigma deviation of the median) for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively, are $0.080\% \pm 0.006\%$ (or $0.035\% \pm 0.003\%$ for elementary P), 0.267 ± 0.037 , 0.089 ± 0.017 , 0.049 ± 0.006 and 0.021 ± 0.002 . *These figures can be considered our Clarke estimates for silicites*, which turned out to be noticeably lower than Ronov’s figures.

It is characteristic that the phosphorus content in silicites is much higher than in carbonates (P_2O_5 0.08% vs. 0.05%), although it would seem that both carbonate and siliceous matter should be initially sterile in phosphorus. Nevertheless, phosphorus anomalies are found even in non-carbonaceous highly siliceous rocks, in which there are no or almost no such common phosphorus concentrators as organic, clay or hydroxide matter. This suggests that the phosphorus ab-

sorber could sometimes be and the siliceous sediment itself. The ability of hydrated amorphous silica to absorb phosphate seems quite likely (although we do not know experimental data of this kind)⁸, but this requires an increased concentration of phosphate in the bottom water. There is no such condition in the photic zone, where the content of dissolved phosphate due to photosynthesis of living matter can fall to analytical zero. But it can be realized in deep waters, on which the happy idea of A.V. Kazakov (1939) about upwelling was based. *Since a significant part of the silicites is deep-sea formations, their frequent enrichment with phosphorus seems quite natural.*

As among carbonate rocks, mixed rocks are distinguished by increased phosphorus content—most often clay-siliceous. In such rocks, phosphorus antagonism with silica and positive correlations of phosphorus (or phosphorus modules) are usually detected either with clay components aluminum and titanium, or with iron hydroxide, or with both. This means that the carrier of phosphorus in silicites and clay silicites is a clay and hydroxide substance. However, the natural picture of the geochemistry of phosphorus in silicites is far from simple, since sometimes there is a negative correlation of phosphorus with a clay admixture.

Phosphorus accumulation is noted in silicites associated with the volcanogenic hydrothermal ore process, for example, in pyrite deposits of the Southern Urals [42] or in Famen manganese-ore carbonate-siliceous “phthanitoids” of Pai-Khoi [43]. Among the rarer cases of correlation is the positive relationship of phosphorus with the normalized alkalinity of NaCaM, which may indicate the tuffogenic nature of phosphorus in such silicites.

8.5. Carbonaceous Biolithes

This section presents in abstract form our essays on the geochemistry of phosphorus in carbonaceous biolithes of two types—black shales containing organic matter mainly of the “sapropel” type, and in coals containing organic matter mainly of the humus type. The reader can find references in the works used [34] [35] [36] [46], in the text of the monograph they are replaced by angle brackets (<...>).

More than a quarter of a century ago, we made the following conclusions regarding *the geochemistry of phosphorus in black shales* ([34], p. 202):

1) Clarke phosphorus content in black shales, estimated by various methods, is 1800 - 1500 ppm, or 0.4% - 0.3% P₂O₅. The contents of P₂O₅ > 0.5% can be considered abnormal. Thus, the Clarke content of P₂O₅ in black shales is three to four times higher than in non-carbonaceous sedimentary rocks. Siliceous and terrigenous black shales are richer in phosphorus than carbonate shales. In the context of the stratisphere, the most phosphate-bearing in general were those black shales that are associated with *stratum phosphorites*: Upper Cretaceous,

⁸Only experimental data by Harder [44] are known—on the sorption of dissolved silica and phosphate on aluminous hydroxides, which well explains the formation of phosphate-containing glauconite [45].

Permian, Cambrian.

2) Two genetic lines can be traced in the genesis of phosphate-bearing black shales: a) sediments of long-stagnant basins; b) sediments of ancient upwelling zones. In addition, the accumulation of phosphorus in bone detritus and fecal material plays an important role in “condensed” black *domanicoïd shales*. In accordance with the well-known scheme of G.N. Baturin [4], for the majority of phosphate-bearing black shales, the processes of natural enrichment (dressing) with the accumulation of phosphate during precipitation washing were of significant importance.

3) In the formation of carbonaceous silts, the proportion of fossilized biogenic phosphorus P_{bio} is many times less than the proportion of P_{org} : significant (and possibly even prevailing, giving up to 80%) part of the P_{bio} is regenerated into the bottom waters at the earliest stage of diagenesis. It is this long-known fact that turns out to be key to understanding the spatial relationships of black shales with stratum phosphorites. We assume that this relationship is not only paragenetic (members of a single facies series described by E.A. Yeganov [47] [48]), but also partly genetic. Its essence is that the facies of carbonaceous sediments served as an intermediate phosphate collector, feeding deep waters with it and thereby creating a phosphorus reserve for the formation of future stratum phosphorites.

4) It is assumed that the main mechanism of formation of formation phosphorites was not the chemical deposition of calcium phosphate in the carbonate system, which has serious thermodynamic limitations, but the metasomatic substitution of francolite for various carbonate sediments. Among the latter, as the studies of E.A. Yeganov [49] show, there were a lot of riphogenic.

In this paper, correlations of phosphorus or phosphorus modules in some samples of black shales were additionally investigated. It turns out that the overall picture of correlations is far from simple and often paradoxical. Only in young black shales or sediments was a significant positive correlation of phosphorus (or phosphorus modules) revealed with C_{org} , which means that the phosphorus carrier was the OM buried in the former carbonaceous sediments. In most metamorphosed Precambrian black shales, there is no special specificity; phosphorus shows the same correlations as in non-carbonaceous rocks, for example, with titanium, iron or calcium.

At the same time, unusual, strange correlations have been revealed in black shales—for example, the antagonism of phosphorus with the components of the former clay substance, reflecting the complex processes of phosphorus migrations during lithogenesis and metamorphism of carbonaceous sediments.

As for the *geochemistry of phosphorus in coals*, the generalization of a significant amount of data ([35], p. 193-207) allowed us to draw the following conclusions:

1) The biophilic element phosphorus is moderately “coal-file”. Its coal Clarkes are 220 (ash), 30 (coal) and 270 (ash), 20 (coal) ppm for brown and hard coals, respectively. Ash Clarkes are 2.2 times higher than the Clarkes of sedimentary

rocks. The Clarke distribution of phosphorus is characterized by a significant dispersion: there are coals enriched with phosphorus 8 - 10 times against general Clarke. Usually there are phosphates of Ca, Al or Fe in such coals.

2) In most coals, phosphorus is distributed as a typical “coal-file” element; its contents in coals grow non-linearly with an increase in ash content, passing through a maximum in a certain ash content interval, and in ash, on the contrary, decrease. This distribution, as well as the data of phase analyses, proves the presence of two forms of phosphorus in coals—organic (P_{org}) and mineral (P_{min}). In low-phosphorous and low-ash coals, P_{org} dominates, and in high-phosphorous coals, P_{min} dominates. As part of the P_{org} , the leading role belongs to the virtual sorption fraction of P_{sorb} and the secondary one is the biogenic fraction of P_{bio} . An increase in the contribution of the latter can probably be expected in liptobolite coals. For phosphorus, the concept of sorption fraction is not the same as for metals. P_{sorb} is not a compound of phosphorus with peat or coal, but phosphorus associated with ash-forming components of sorption ash—Ca, Mg, Fe, Al.

3) The most characteristic feature of the geochemistry of phosphorus in coals is its removal during coal formation. Evidence in favor of this is: a) an order of magnitude lower phosphorus content in coals compared to modern peat; b) accumulation of P in soil, roof and parting rocks observed in many basins; c) concentrations of P in the coal seam at the contacts of coals of different petrographic composition and ash content, and especially at contacts with near-coal rocks; d) thermodynamic statistical data on the instability of syngenetic phosphates in the diagenesis of a peat formation, which should cause the migration of phosphorus from coals to the nearest alkaline barriers—into the roof, soil or into partings.

4) The features of the composition of P_{sorb} and the high mobility of P in diagenesis make it possible that the forms of phosphorus during coal formation can significantly change towards an increase in the contribution of the form of P_{min} compared with the form of P_{org} as the coal metamorphism increases.

5. The genesis of at least a part of high-phosphorous coals is associated with syngenetic processes of enhanced phosphorus introduction into paleo-peats. The source of phosphorus could be both terrigenous and volcanogenic clastics.

8.6. Weathering Crusts and Associated Ores

In this section, the phosphate content of weathering crusts and associated Al ores (bauxites), Fe-Al ores and essentially Fe ores (for example, those formed on the substrate of Precambrian ferruginous bauxites) is considered. “Bauxites” we called alumina rocks with an aluminosilicon modulus $AM (Al_2O_3/SiO_2) > 2$. Accordingly, we attributed the so-called “siallites” (AM less than 1) and “allites” (AM from 1 to 2) to weathering crusts. Fe-Al ores were called such alumina rocks in which the value of $Fe_2O_3 + FeO$ exceeded 20%; therefore, many so-called “ferruginous bauxites” turned out to be here. Fe ores included formations rich only in iron, but not in alumina. Finally, some Fe ores are also enriched with manganese, and some bauxites are enriched with titanium. *All these formations are*

genetically closely related, so the boundaries we have adopted between them are very conditional.

As for phosphorus, its behavior during weathering is mainly determined by the pH of the medium. So, in his review, Yu.P. Kazansky attributed apatite to minerals “moderately resistant” to chemical weathering processes ([50], p. 29), and referring to D.L. Askinazi (1949) noted that the maximum dissolution of soil phosphates was observed at acidic pH, lower 4.0 - 4.5 ([50], p. 44). According to a later review by Yu.N. Zanin and V.I. Ternovoy ([51], pp. 24-26), the behavior of phosphorus in weathering crusts was also determined mainly by the acidity of the medium. The conclusion of Yu.N. Zanin and V.I. Ternovoy on the behavior of phosphorus in laterite weathering crusts generating bauxite and ferruginous bauxite is especially important ([51], p. 25):

“In laterite weathering crusts characterized by the development of aluminum and iron phosphate minerals, phosphorus is one of the least mobile elements, often as stable as Al or Ti, in most cases less mobile than Si^p. If the formally calculated removal of phosphorus from laterite weathering crusts turns out to be higher than the removal of Si, it can be assumed that this took place before significant lateritization of the rock.”

Data of **Table 5** and consideration of all available materials allow us to draw several conclusions:

1) The average median ($Me \pm 2\sigma_{Me}$) values for the totality of all weathering crust formations obtained on the basis of 205 samples are 0.150% \pm 0.016% for P₂O₅, PTiM, PCaM, PFeM and PFe(t)M, respectively (or 0.066% \pm 0.007% for elementary P), 0.127 \pm 0.052, 0.160 \pm 0.042, 0.018 \pm 0.004 and 0.013 \pm 0.003. *These figures can be considered our estimates of Clarkes for weathering crusts and associated ores.*

Thus, with a large averaging of the phosphorus content in the formations of the crust, the weathering is approximately comparable to those in the pelites (0.150% P₂O₅ versus 0.140%). This means that during the formation of weathering crusts, the processes of accumulation and removal of phosphorus are approximately balanced (but with a preponderance towards removal)—depending on the fluctuations of the Eh medium and the presence or absence of newly formed phosphorus sorbents.

2) During the formation of bauxites, phosphorus definitely accumulated: the average content of P₂O₅ in bauxites is noticeably higher than in other alumina or ferruginous weathering crusts: 0.155% vs. 0.120%. However, there is no more phosphorus in Al-Fe and Fe ores than in pelites (0.129% P₂O₅).

3) At the initial stages of the formation of weathering crusts, phosphorus can positively correlate with the components of hydrolysate sorbents-carriers: titanium, aluminum, iron oxide.

4) However, with a far-reaching laterite process (*i.e.* already in bauxites, Al-Fe and Fe ores), a negative correlation of phosphorus with hydrolysate components,

⁹Highlighted by us.

in particular, with aluminum, was noted. This correlation indicates that the phosphatization of weathering crust formations occurred later than the formation, as well as for iron-manganese ores in the bauxite-bearing strata of the Angara-Yenisei province.

8.7. Tuffoids

As is known ([1], p. 350), in lithology, there are varieties of volcanogenic-sedimentary rocks: ash tuffs, tuffites, various kinds of “tuffogenic” rocks (for example, tuff sandstones or tufo-argillites) and volcanomictic rocks. The first three contain pyroclastics material; in tuffs it predominates, and in others it is more or less an impurity. The last group contains an admixture of volcanic debris; sandstones are most often so called, but in principle any sedimentary rocks (even carbonate ones) can be “volcanomictic” if an admixture of volcanic rock fragments got into them at the stage of formation of the initial sediment. It is clear that to distinguish the rocks, having at the stage of sedimentation a hot pyroclastics of approximately the same age with sediment, from rocks with cold volcanoclastics, which can be hundreds of millions of years older than sediment. Such distinction is possible only in sedimentites, little changed by secondary processes. In this case, volcanoclastics is easily distinguished from pyroclastics by the rolling of the grains.

However, very often a geologist deals with rocks changed in catagenesis or even in metamorphism; therefore, accurate diagnosis of volcanogenic sedimentary rocks is difficult, and often simply impossible. In order to distinguish tuff from tuffite, tuffogenic or volcanomictic rock, a geologist requires imagination rather than precise knowledge. It is no coincidence that a number of such diagnoses in V.T. Frolov’s monograph [52] were subjected to scathing criticism.

All of the above is the basis for the use of the term of free use proposed by us – *tuffoids* [28]. All rocks with a “noticeable” admixture of volcanogenic material were classified as such. Noticeable—meant “one that gives the chemical composition of rocks a certain lithochemical anomaly”. For example, almost all pseudo-hydrolysates and pseudo-siallites turn out to be either simply basaltoids or basitic tuffoids; their increased magnesia is most often explained by an admixture of chlorite—a derivative of dark-colored minerals (olivine, pyroxenes, amphiboles, biotite). These are the majority of *sypherlites* (increased iron modulus FeM with GM, characteristic of syallites), and many alkalites (compositions with an amount of alkalis greater than 8%). *Elevated phosphorus levels can also be considered one of the diagnostic signs of tuffoids, inherited by them from the original volcanic rocks or volcanic ash.*

As shown in **Table 6**, the median values (approximately with a two-sigma deviation of the median) for P_2O_5 , PTiM, PCaM, PFeM and PFe(t)M, respectively, are $0.150\% \pm 0.014\%$ (or $0.066\% \pm 0.006\%$ for elementary P), 0.197 ± 0.020 , 0.052 ± 0.009 , 0.049 ± 0.005 and 0.023 ± 0.002 . In view of the initial extreme heterogeneity of the tuffoid population, it is quite clear that there is no question of any Clarke assessment of tuffoids.

Table 6. Phosphorus content and the value of phosphorus modules in tuffoids of different composition.

Rocks	n	N	P ₂ O ₅ , %	P, %	PTiM	PCaM	PFeM	PFe(t)M
Hyperbasites	13	32	0.140 ± 0.065	0.062 ± 0.029	0.093 ± 0.027	0.028 ± 0.020	0.042 ± 0.023	0.012 ± 0.009
Basites	72	291	0.170 ± 0.026	0.075 ± 0.012	0.143 ± 0.024	0.032 ± 0.012	0.033 ± 0.010	0.018 ± 0.003
Mesites	81	348	0.160 ± 0.021	0.070 ± 0.009	0.222 ± 0.029	0.059 ± 0.012	0.056 ± 0.008	0.026 ± 0.004
Acidites	58	259	0.100 ± 0.016	0.044 ± 0.007	0.218 ± 0.038	0.083 ± 0.023	0.060 ± 0.012	0.027 ± 0.006
All tuffoids	224	930	0.150 ± 0.014	0.066 ± 0.006	0.197 ± 0.020	0.052 ± 0.009	0.049 ± 0.005	0.023 ± 0.002

Note. n is the number of samples, N is the total number of analyses.

Some idea of the quantitative characterization of this heterogeneity is given in **Table 6**, in which estimates of phosphoricity indices are given for four groups of tuffoids, completely conditionally distinguished by the content of SiO₂—hyperbasitic, basitic, mesitic and aciditic. The conventionality of such a grouping is that with a small fraction of pyroclastics in a given tuffoid (for example, in a substantially psammite or silicite rock), the SiO₂ content will be determined precisely by the composition of the initial host sediment, and not by the composition of the pyroclastics buried in it.

At the same time, almost all the samples are “hyperbasite” tuffoids (11 out of 13) are certified as alkaline (>1% - 2% of alkalis), in the group of “basite” tuffoids, alkaline (>4.5% of alkalis) account for a third of all samples (22 out of 72), among “mesite” tuffoids, the proportion of alkaline (>7.8% of alkalis) is about one-eighth (11 out of 81), and in the group of “acidite” tuffoids (>9% of alkalis) there are very few alkaline varieties (two samples out of 60). Summarizing the data and calculations in **Table 5**, **Table 6** allow us to draw several conclusions:

1) Volcanism is certainly one of the important factors of phosphogenesis. This idea of Academician N.S. Shatsky was once challenged by Academician N.S. Strakhov. But the groundlessness of these doubts was shown not only by N.G. Brodskaya [9] and other followers of N.S. Shatsky, but also reliably proved by a number of other authors, and especially by the latest balance calculations of our largest phosphorite—G.N. Baturin¹⁰.

2) The materials collected by us also leave no doubt about the important role of volcanism for phosphogenesis. The most convincing evidence of this is the existence of regionally aged *phosphorous geochemical horizons of volcanogenic nature* ([53], pp. 62-80).

3) At the same time, the phosphorus content and the values of phosphorus modules in volcanogenic sedimentary rocks (tuffoids) are subject to strong variations. These variations are controlled by at least three factors: a) the composition of the pyroclastics, including its alkalinity; b) the composition of the host sediment, the background phosphoricity of which could be completely different for psammite, pelite, silicite or carbonate sediments; c) the ratio in a particular

¹⁰Baturin G.N. Bioproductites and volcanism//Dokl. RAS. 2009. Vol. 426. No. 5. pp. 653-657.

tuffoid between the former host sediment and pyroclastics—from a small admixture of the latter to the predominance in real tuffits.

4) The division of tuffoids into four conditional groups according to silica content, followed by the calculation of the average values for each group allowed us to establish that the maximum median phosphorus content ($P_2O_5 = 0.170\%$) is possessed by “basite”, and the poorest are “acidite” tuffoids ($P_2O_5 = 0.100\%$). The greatest value of the phosphorus-titanium module (PTiM) is shown by titanium-poor mesite and acidite tuffoids. The values of the other three modules (PCaM, PFeM and PFe(t)M) are maximal in the group of “acidite” tuffoids, the poorest in both calcium and iron.

5) Along with the usual correlations of phosphorus and phosphorus modules—with titanium, calcium, iron (often nitrous) and alkalis, tuffoids are characterized by the presence of strange, paradoxical correlations, for example, negative correlation with titanium, aluminum, iron and positive correlation with silicon.

6) Another typical feature of tuffoids can be considered the often manifested positive correlation of phosphorus or some phosphorus modules with sodium. It can be assumed that the introduction of albite pyroclastics into the sediment was accompanied by the introduction of volcanogenic phosphorus.

8.8. Other Lithotypes

This section includes silicate analyses characterizing nodules and “*concreoid*” [54], including phosphate and phosphate-containing ones, as well as carbonate and more specific siliceous silicate and sulfide-silicate nodules prevailing in sedimentary strata, and sometimes even former nodules in the composition of metamorphic strata. A small number of complete analyses of evaporite rocks—chloride or sulfate—can also be found in the literature. Of the listed lithotypes for phosphorus geochemistry, the most important, of course, are phosphate and phosphate-containing nodules, which are discussed in more detail in Chapter 8: “*Lithochemistry of phosphorites*”. In most essentially carbonate nodules, there is also some accumulation of phosphorus. In other lithotypes, phosphorus usually does not accumulate.

The presented materials allow us to draw several conclusions:

1) *The diagenetic process of nodule formation plays an absolutely exceptional role in the hypergenic geochemistry of phosphorus.* Practically all phosphorite deposits are composed of substantially phosphate nodules—either macro- (nodular phosphorites) or micro-nodules (stratum phosphorites).

2) Long-term discussions of phosphorite specialists have led, it seems to us, to an agreement regarding the genesis of “grains” or “pellets” in stratum phosphorites: most experts tend to consider these micro-concretions as bacterial formations.

3) In addition to substantially phosphate, other nodules, and among them the predominant ones in the stratisphere are substantially carbonate, are enriched with phosphorus in comparison with non-concretionary carbonates or marls. In

any case, when studying the Paleozoic strata of the Pechora Urals [37], the presence in the analysis of a more undefined carbonate formation of elevated phosphorus and manganese contents made it possible to accurately identify the rock as a concretion or concreoid.

4) A special place among nodule formations is occupied by phosphate-containing essentially *berthierine* (previously mistakenly called shamosite) nodules of two genotypes: a) associated with the removal of iron from closely located weathering crusts on the continent and b) formed from basalt or andesite pyroclastics buried in sediment [55]. A spectacular example of the latter are the beautiful “Sochi balls” [56], in which the phosphorus content can reach the conditions for phosphorites.

5) Due to the huge variety of nodules and their characteristic variability of mineral composition, even within the same group [43], as a rule, it is not possible to notice significant correlations of phosphorus or phosphorus modules with nodule-forming components.

6) Among rare lithotypes (for example, mainly sulfate, anhydrite or such as dawsonite), there are no noticeable accumulations of phosphorus, and among the correlations there were positive associations with iron oxide (phosphorus collector) and negative ones with normalized alkalinity of NaCaM ($\text{Na}_2\text{O}/\text{K}_2\text{O}$).

9. Lithochemistry of Phosphorites¹¹

The materials presented in this chapter allow us to draw several conclusions:

1) The first experience of applying lithochemistry to phosphorites, undertaken 20 years ago [28], turned out to be encouraging, since it allowed us to draw several non-obvious genetic conclusions: about the presence of hydrolysate materials (probable phosphorus sorbents) in phosphate rocks, about arid and even evaporite facies of phosphate accumulation, and a number of other equally non-trivial ones.

2) Along with this, it turned out that phosphorites are very specific formations, so standard lithochemical analysis does not always lead to success. Instead of the usual modular diagrams, such as, for example, “Alkali - GM”, simple ratios involving phosphorus were more effective: $\text{CaO} - \text{P}_2\text{O}_5$ and $\text{Fe}_2\text{O}_3 - \text{P}_2\text{O}_5$, reflecting the main features of the mineralogy of phosphorites. For a more meaningful interpretation of the lithochemical features of phosphate-containing rocks, modules were used that additionally characterize the bonds of phosphorus with titanium, calcium and iron (see above). This technique provides an objective division of analytical sets into clusters, *i.e.* varieties of phosphate-containing rocks and high-percentage phosphorites.

In the book, lithochemical clustering of silicate analyses was carried out for seven large groups of phosphate-containing rocks: Pre-Riphean, Riphean-Vendian,

¹¹The predominant part of this chapter was published in a separate issue of the Ural Geological Journal (2019. No. 3 (129). 86 pp.). In the monograph, the presentation is slightly supplemented with materials that did not get into the specified publication.

Vendian-Cambrian, other Paleozoic, Mesozoic and Cenozoic, the youngest and phosphorite weathering crusts formed by phosphate-containing substrates of different ages.

3) Archean and Proterozoic metamorphites enriched with apatite, representing metamorphosed ancient phosphorites, are described on the Voronezh crystal massif, on the Baltic and Aldan shields. In the first region, phosphate content is closely associated with black shales, in others there is no such association. Lithochemical analysis of high-carbon, sulfide-rich black shales of the Lower Proterozoic Tim formation in the Voronezh massif revealed a positive correlation of phosphorus with titanium (especially with the titanium module TM), iron, sulfide sulfur and carbon. Together, these connections support the idea of a volcanogenic source of phosphorus in a large Early Proterozoic (Karelian) sedimentary basin on the territory of the KMA.

4) In the Upper Riphean phosphate-boxites on the Timan, the correlation of phosphorus with calcium is rather weak, but there is a significant negative correlation with sodium, and the PFeM modulus is negatively correlated with potassium and positively with the hydrolysate modulus of GM; all this indicates the relationship of phosphate content with the process of ancient weathering of Riphean black shales. In the 10 deposits of Ediacaran phosphorites studied by A.V. Ilyin [57] [58], which are often carbonaceous, in the presence of a positive correlation of phosphorus with calcium, there is no connection with fluorine, moreover, for the PCaM module it is even negative. Phosphorus is negatively correlated with carbonate content, and the PCaM modulus is negatively correlated with magnesium. Such correlations may indicate metasomatic phosphogenesis: phosphate substitution of the carbonate matrix.

5) In the “aphanite” (micrograin) phosphorites of the Vendian-Cambrian, unique due to their primary sedimentation (and not diagenetic) genesis [59], studied on the example of the Kharanur deposit of the Khubsugul basin, phosphorus is positively strongly correlated with CaO and, as a consequence, negatively with most of the other components, most strongly with SiO₂. At the same time, phosphorus, and especially the PCaM module (*i.e.* apatite phosphorus) are negatively correlated with carbonate content, which almost certainly indicates the mechanism of phosphogenesis: in this case, obviously, metasomatic substitution of carbonate with phosphate.

6) The Cambrian Kuonama strata of the Siberian Platform is characterized by increased manganese content (an indication of the presence of carbonates) and high carbon content. Rocks of some cluster varieties are highly ferruginous, which sometimes leads to the certification of rocks such as phosphate hydrolysates. In typical Cambrian phosphorites of the Karatau basin, phosphorus (and the PFeM module) is strongly positively correlated with CaO and, of course, with fluorine, and negatively with alkalis. These correlations are enhanced by the heterogeneity of the analytical set: the presence of two compositions (Janatas and Chulaktau districts) with the highest silicity (34% - 39% SiO₂) and the lowest phosphateness (16% - 18% P₂O₅).

7) In the composition of the Middle Ordovician (Lower Karadok) shell phosphorites in the Podkamennaya Tunguska basin, there is a close correlation of calcium with phosphorus, reflecting the dominance of apatite (francolite) in the composition of phosphate matter. In the composition of Silurian phosphate-bearing black shales on the Pai-Khoi, in addition to the obvious connection of P_2O_5 - CaO, there is a complete absence of other positive correlations of phosphorus, with an abundance of negative ones, of which the strongest is with SiO_2 . This may indicate the mechanism of phosphogenesis: substitution of silica with phosphate, probably in early diagenesis.

8) As part of the Devonian, very peculiar “fish phosphorites” in the Middle and Northern Timan, four varieties were identified—clusters that differ in carbonate content, clay and sandiness, which is reflected in the phosphate content. Among the correlations of phosphorus is the usual positive for phosphorus with CaO and negative with SiO_2 , Fe_2O_3 , as well as a very unusual for phosphorus geochemistry—a negative correlation with TiO_2 .

9) Even the usual correlation of P_2O_5 - CaO is insignificant in the composition of Visean siliceous phosphate-bearing black shales on the Pai-Khoi, which may indicate the entry of phosphorus into organic matter. Positive correlations of P_2O_5 with alkalis and with femicity are more definitely recorded. In the phosphorite nodules (also carbonaceous) lying in these shales, correlations of the PFeM module appear: positive with CaO and negative with SiO_2 . Carbonaceous phosphorite nodules also occur in the C_2 - C_3 limestones higher up the Pai-Khoi section. In addition to the usual P_2O_5 - CaO bond, the complete absence of other positive correlations of phosphorus is remarkable, in the presence of negative ones, of which phosphorus has the strongest with SiO_2 , and the PCaM module has MgO. This may indicate the mechanism of phosphogenesis: phosphate substitution of siliceous and carbonate sediment, probably in early diagenesis.

10) The Medium Carbon—Lower Permian phosphorites of the South Ural basin are a product of phosphatization of reef limestones and siliceous sediments in the anoxic deep-water “pre-flisch formation” [60], and the phosphatization of carbonates could be combined with Mn accumulation. The clearest correlations of phosphorus are negative with carbonate content and positive with manganese. For some of these phosphorites, high values of the hydrolysate modulus (GM) are very characteristic, due to the processes of late weathering of reefs in a sub-aerial environment, with the accumulation of hydrolysate (ferruginous or alumina) components—possible phosphorus collectors.

11) Lithochemical processing of a large number of analyses of phosphorites in the siliceous member of the formation of Phosphorium in Permian black shales (Retort Phosphatic Shale Member) [25], published by R. Gulbrandsen (1966), showed significant uniformity of the analytical data, which makes the selection of cluster varieties conditional to a certain extent. Phosphorus (and the PFeM modulus) strongly positively correlates with CaO and, of course, with F, and P_2O_5 negatively correlates with silicate components: SiO_2 , Al_2O_3 , TiO_2 and alkalis; but the strongest negative correlation of the PCaM modulus is with carbo-

nate content. Very close (almost functional) connection of CaO - P₂O₅ in the context of state Idaho means the complete dominance of apatite phosphorus, which is quite consistent with the shell nature of these phosphorites.

12) In the composition of the Jurassic-Cretaceous zhelyak (=nodul) phosphorites of the Russian platform studied by V.Z. Bliskovsky [6], in addition to the usual close relationship of P₂O₅ with CaO and F, a negative correlation of P₂O₅ with SiO₂ is observed. Lithochemical treatment of the compositions of phosphatized psephites from different deposits [16] revealed the presence of a rare chemotype—*phosphate sypherlite*, which reflects the important role of iron oxide in the formation of nodular phosphorites—especially with their usual correlation with glauconite. Iron oxide, as a probable primary sorbent of phosphorus, was carried into the coastal shallow water during erosion of the weathering crust on nearby land [45] [61]. Lithochemical clustering of the compositions of modified phosphorites at the Chilisai deposit of the Aktube basin showed the absence of the usual phosphorus-calcium bond, which indicates the removal of phosphorus as the phosphorites are weathered.

13) Lithochemistry of phosphate-containing rocks found in the Indian Ocean has shown, in addition to the expected positive correlation of phosphorus with calcium and fluorine, there is also a correlation with manganese, and a negative one with SiO₂, MgO and carbonate content.

14) Extensive materials on weathering crust phosphorites, generalized worldwide in 1975 by Yu.N. Zanin [62], and in the Polar Urals region in 2006 by V.I. Silaev [63], showed the extreme complexity of phosphorus behavior during the formation of weathering crust. In these processes, the following could occur: a) removal of phosphorus from the weathering crust, b) residual concentration of phosphorus in the weathering crust, c) redistribution of phosphorus in the weathering crust, accompanied by both its removal and introduction (secondary concentration) [5] [6] [64]; therefore, lithochemical studies reveal a wide variety of correlations of P₂O₅ and phosphoric modules in phosphorites formed in weathering crust by different-age phosphate-bearing substrates.

15) For a number of lithochemically studied phosphorites, in addition to the usual correlation of phosphorus with calcium, a positive correlation with sodium is also revealed, indicating the entry of sodium into the phosphate structure, *i.e.*—the dominance of francolite.

10. Typification of Phosphorus Concentrations in the Stratisphere

The extreme diversity of phosphorus concentrations in sedimentary rocks creates an urgent need for their typification. Such a typification is highly desirable, which would also have some “practical significance”—it would allow predicting one or another type of concentrations in unexplored areas or sedimentary rock strata not covered by analysis. This chapter describes 11 genotypes of phosphogenesis [65], which are partly independent, partly have overlapping areas, shown in **Figure 3**.

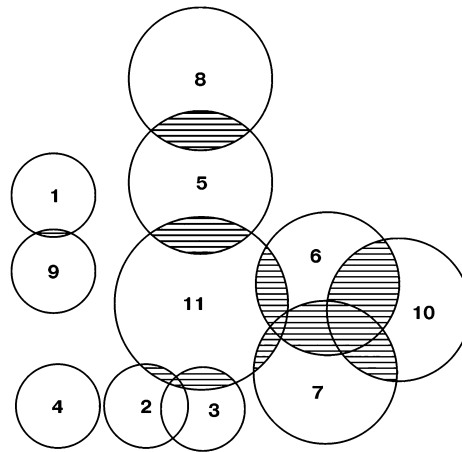


Figure 3. Ratios of phosphogenesis genotypes shown by Leonhard Euler circles. The areas of subject overlaps are shaded. Genotypes: 1—peat vivianite, 2—black shale diagenetic, 3—skeletal biomorphic, 4—insular fecal, 5—Cambrian and Upper Cretaceous–Neogene metasomatic, 6—above-reef metasomatic, 7—volcanogenic metasomatic, 8—Ediacaran sedimentation, 9—Kerch sorption, 10—hi-atus shlich, 11—hypergenic, weathering core.

1) It follows from the description of genotypes that in epigenetic genotypes 9 and 10 there was a previous “ore preparation stage”, *i.e.* the creation of syngenetic, but non-industrial concentrations of phosphorus, which in epigenesis are enriched to an industrial level. However, in syngensis, in addition to “pure lines” of genotypes, “crossing lines” are quite real, *i.e.* sets of two or even three genotypes, for example:

1 + 9 = formation of vivianite both in swamps and in iron ores of the Kerch type;

2 + 3 + 6 = phosphoric “respiration” of depressive carbonaceous silts (where diagenetic phosphorite-formation occurs) splashes out to the periphery of the depression, where there is either a reef or carbonate sediments, and phosphorus settles on the Ca barrier;

6 + 7 = volcanogenic phosphorus settles not in carbonaceous sediment, but on the reef Ca-barrier;

5 + 8 = dissolved phosphorus produces metasomatic phosphatization of carbonate or siliceous sediment in diagenesis, or calcium phosphate is precipitated directly (most often with subsequent redistribution in diagenesis), etc.

2) With the exception of the late-epigenetic genotype 11, the remaining genotypes can be combined into two groups according to the source of phosphorus: a) directly related to organic or mineral biogenic substance, *i.e.* with P_{bio} ; b) “non-personalized” phosphorus, which has no direct connection with P_{bio} . In these groups, the concentration of phosphorus occurred according to two scenarios.

The first scenario can be conditionally called dynamic; it is characterized by “Baturin cycles”, reflecting frequent fluctuations in the value of Eh during sedi-

mentation, periodically accompanied by erosion of the sediment with the formation of a slurry. Such a scenario generated industrial deposits of nodular phosphorites.

The second scenario can be called sedimentary-diagenetic. It is characterized by diagenetic phosphatization of carbonate (and less often siliceous or ferruginous oxide) sediments, as well as direct accumulation of calcium phosphate in Ediacaran genotype No. 8. Such a scenario generated industrial deposits of formation granular and micro-granular phosphorites (including “aphanite”), as well as deposits of phosphate-containing iron ores.

In this phosphogenesis scenario, two variants can also be distinguished by the assumed primary source of phosphorus: a) oceanic (Ediacarian and Cambrian phosphorites) and b) terrigenous (Cretaceous-Paleogene phosphorites).

11. Five Genetic Correlations of Phosphogenesis in the Stratisphere¹²

The genesis of phosphorites, as the analysis of numerous publications shows, in the modern geochemistry of hypergenesis still remains the most difficult, not completely solved problem. It is only possible to indicate several factors correlating in one way or another with the genesis of phosphorites: climate, volcanism, dynamic facies, hydrochemical facies and the presence of glauconite.

Correlation of phosphogenesis and climate

Since biota (in particular, marine biota) is the most powerful phosphorus concentrator in the hypergenesis zone, and the functioning of biota strongly depends on the phosphorus content in water or soil, the correlation of phosphogenesis with climate seems necessary.

As N.M. Strakhov (1960) and later A.L. Yanshin (1986) showed, the main deposits of phosphorites were formed in a hot arid climate. A particular consequence of this correlation is the parasteresis and even paragenesis of phosphorite-bearing basins with evaporites—an idea that was vigorously developed by A.L. Yanshin [19].

In addition to isoclimaticity, the correlation of phosphogenesis with evaporites could be enhanced due to huge upwelling occurring at the boundaries of phosphate-bearing and evaporite facies.

However, there is also a paradoxical connection of phosphogenesis not with a hot, but, on the contrary, a cold climate—in the epochs of glaciations, which were either polar (in Perm) or global (in the Pre-Ediacaran epoch). Polar glaciations (the idea of R. Sheldon, 1984) also generated powerful upwelling, and global (Marinoan)—contributed to the accumulation of huge masses of phosphorus in the ocean waters under the ice, which gave rise to large deposits of stratum phosphorites in Ediacaria and Cambria (the idea of A.V. Ilyin, 2008 [57]).

Correlation of phosphogenesis and volcanism

¹²The material of this chapter was published in 2019 [61].

Signs of the influence of volcanism on the formation of phosphorites or phosphate-containing rocks may be: 1) geochemical anomalies of phosphorus, obviously hydrothermal in nature; 2) facts of phosphatization of atolls; 3) association of phosphorites with hydrothermal iron hydroxides; 4) the presence of phosphate-containing silicate-siliceous nodules in rocks (which may have another genesis); formation of extended phosphoric geochemical horizons—in cases when it is caused by subsynchronous volcanism. Volcanogenic geochemical horizons are recorded at various stratigraphic levels of the stratosphere, but are most characteristic of ancient strata.

Unlike elements such as iron and manganese, the connection of phosphoric geochemical anomalies with volcanism is very much masked by the processes of biogenic phosphorus concentration; this is why all the difficulties of identifying such a connection.

Nevertheless, in recent years, the idea of N.S. Shatsky about the connection of phosphogenesis with volcanism has been receiving new confirmations—even from former, very authoritative opponents of such a connection—for example, such as our largest phosphorite-expert G.N. Baturin.

Correlation of phosphogenesis and dynamic sedimentation facies

Morphology and composition of phosphorites or phosphate-containing rocks are often combined with dynamic facies of sedimentogenesis. Signs of the influence of dynamo-facies on the formation of phosphorites or phosphate-containing rocks may be: 1) low sedimentation rate; 2) the presence of breaks and natural sludge in the section of the phosphate-bearing strata; 3) evidence of past currents and upwellings.

In particular, the indicators of highly dynamic facies can be the concentration of phosphate nodules or bone residues associated with periodic erosion and the formation of hardgrounds with the formation of so-called “Baturin cycles”.

Correlation of phosphogenesis and anoxic facies of sedimentation

The available materials on the connections of phosphogenesis with anoxia allow us to make some generalization, namely, to distinguish two cases of anoxia [66].

In the first case (shelf upwelling), phosphogenesis is not genetically related to anoxia. Here the increased the bioproductivity of surface waters (an increased value of factor P [34]) generates two consequences: 1) the occurrence of anoxia in bottom waters due to the consumption of oxygen for the oxidation of unusually abundant organic matter; 2) an increase in the concentration of phosphorus in pore waters for the same reason—the decomposition of OM [3].

In the second case, anoxia was global in nature: due to the disruption of ocean circulation, so-called Oceanic Anoxic Events (OAE) occurred (for example, in the Paleo-Atlantic, a number of such “events” are distinguished in the Cretaceous). Here, anoxia was also accompanied by the formation of carbonaceous sediments, but no longer due to an increase in factor P (bioproductivity of surface waters), but due to an increase in the value of factor F, *i.e.* due to increased

fossilization of OM [66], again with the enrichment of pore waters with phosphate [34].

So, only in the second case there is a direct genetic link between anoxia and phosphogenesis (it was anoxia that gave rise to phosphogenesis), whereas in the first case they are only related paragenetically (since both phenomena were generated by the same factor—upwelling).

An important drain of phosphorus dissolved in coastal anoxic waters, without which phosphogenesis is impossible, are iron oxide hydroxides removed from the weathering crust on the coastal land. In addition to Fe(III) hydroxides, Al hydroxides can also be another drain of dissolved phosphate. However, there is a significant difference between these two types of geochemical barriers for phosphorus: unlike Fe-hydroxides, Al-hydroxides are “indifferent” to anoxia and will not give up phosphorus trapped in weathering crusts when it enters anoxic sedimentation basins.

Correlation of phosphogenesis and the presence of glauconitis

The given information allows us to draw a scenario explaining the long-known paragenesis of phosphates and glauconite. The initial condition for such paragenesis was instability, periodic change of sedimentation and diagenesis environments, which A.E. Fersman shrewdly pointed out back in 1939. Truly, “*the new is the well-forgotten old.*” The modern details of these representations can be shown in the diagram:

Oxidative sedimentation	Reductive diagenesis
The source of phosphate is above-ground water; the high content of Mg^{2+} in it prevents the deposition of Ca-phosphate; therefore, the phosphate formed in diagenesis dissolves. Microconcretionary early glauconitis “matures”—it is enriched with potassium, absorbing it from the bottom water. Fe hydroxides are formed, capturing dissolved phosphate from above-bottom water according to the scheme of the “iron-phosphate conveyor” by P. Frelich <i>et al.</i> , 1988 [67] or T. Algeo and E. Ingalla, 2007 ([68], p. 131).	The source of phosphate is pore waters, where it enters when phosphate-containing Fe hydroxides are dissolved. An early, relatively potassium-poor microconcretionary glauconite is formed, with a high proportion of smectite packets and with Fe^{2+} in the octahedral layers of the structure. This early glauconite absorbs Mg^{2+} from the pore waters, so the formation of Ca-phosphate becomes possible.

So, as all geologists who studied phosphorites believed, the reason for the paragenesis of “phosphates-glauconite” is the commonality of the environments of the formation of glauconite and phosphates. Glauconite is formed under conditions of frequent periodic alternation of topographic and hydrochemical facies, which are characterized by “Baturin cycles”, when the dynamics and, accordingly, the value of Eh of above-bottom waters fluctuate periodically. The position of glauconites on the facies profile of the shelf at a certain distance from the shore and their natural connection with goethite-oolite and berthierine (“shamosite”)

facies clearly indicate weathering crusts (WC)—the most probable source of iron. Iron removed from the WC, most likely in the form of ferrihydrite flakes ([54], p. 30), provided diagenetic formation of glauconite, and ferrihydrite sorbed dissolved biogenic phosphorus, which ensured the subsequent formation of phosphates. *Thus, the direct cause of the paragenesis of phosphorites with glauconite is the close geochemical relationship of phosphorus with iron.*

12. General Conclusion

The paper presents the main conclusions of the Russian monograph “Geochemistry of Phosphorus” (2020).

Based on statistical processing of ~6100 sample averages (from ~190,000 analyses), new estimations of World averages (Clarke values) for P_2O_5 , wt% (and P, wt%), phosphorus-titanium module (P_2O_5/TiO_2), phosphorus-calcium module (P_2O_5/CaO), phosphorus-iron module (P_2O_5/Fe_2O_3), and phosphorus-total iron module ($P_2O_5/Fe_2O_3 + FeO$).

Many estimates have been made for the first time.

In addition to the new Clarke estimates, sometimes very different from previous ones, the work carried out has led to a number of new conclusions. In particular, the titanium geochemical barrier for phosphorus has been first estimated, all the 11 genotypes of phosphogenesis have been named and characterized, five genetic correlations of phosphogenesis have been described, lithochemistry methods have been for the first time successfully applied to characterize the phosphorites.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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