minerals

Article

Clay Mineral Assemblages in the Cretaceous Volcanogenic–Sedimentary Rocks of the North-Western Part of the Transition Zone from the Asian Continent to the Pacific Ocean

Anatoly V. Mozherovsky

V.I. Il'ichev Pacific Oceanological Institute, Far Eastern Branch, Russian Academy of Sciences, St. Baltiyskaya 43, 690041 Vladivostok, Russia; manatoly@poi.dvo.ru

Abstract: In this study, clay and non-clay minerals in the cement of Cretaceous volcanogenic–sedimentary rocks from the bottom of the marginal seas of the north-western Pacific Ocean and adjacent areas were studied. Corrensite and mixed-layer chlorite–smectite, rectorite and mixed-layer illite–smectite, chlorite, swelling chlorite (?), illite, kaolinite, smectite (?), calcite, ankerite, barite, gypsum, epsomite, zeolites (laumontite, analcime, and stilbite), cristobalite, and quartz were determined. The following are the indicative properties: (a) minerals: corrensite and rectorite; (b) associations: corrensite–chlorite, corrensite–chlorite–laumontite, corrensite–epsomite–authigenic calcite, and quartz–illite. Such minerals indicate that the thickness of the accumulated sediments in the studied basins could reach three to five kilometers and that the temperature of their formation could be higher than 150 °C. Transformations in the process of diagenesis and epigenesis occur in two directions: smectite–rectorite–mica, with an excess of potassium, and smectite–corrensite–chlorite, with an excess of magnesium. The chlorite–corrensite association may indicate conditions favorable for seawater evaporation, and the presence of laumontite in the corrensite–chlorite association suggests a periodic supply of calcium to the sedimentation basin. The illite–kaolinite association is probably associated with coal accumulation in epicontinental conditions and a warm humid climate in nearby areas. Periods of sedimentation, possibly associated with global climate events, were identified: 113–120, 110–113, 105–110, 93–95, 72–83 and 61–72 Ma. The established time intervals and mineral associations can serve as benchmarks for stratigraphic constructions in reconstructing the physicochemical, climatic parameters, and conditions of Cretaceous volcanogenic–sedimentary strata accumulation.

Keywords: Cretaceous volcanogenic–sedimentary rocks; authigenic minerals; global climatic events; corrensite; rectorite; illite; chlorite; kaolinite; laumontite

Citation: Mozherovsky, A.V. Clay Mineral Assemblages in the Cretaceous Volcanogenic–Sedimentary Rocks of the North-Western Part of the Transition Zone from the Asian Continent to the Pacific Ocean. *Minerals* **2022**, *12*, 909. https://doi.org/10.3390/min12070909

Academic Editor: Frederick Lin Sutherland

Received: 26 June 2022
Accepted: 19 July 2022
Published: 20 July 2022

1. Introduction

Clay minerals are sensitive indicators of sedimentation conditions, indicating changes in the paleogeographic setting and the nature of the dia- and epi-genetic transformations of sedimentary material. Layered silicates (smectite, corrensite, and rectorite) in association with other minerals have the greatest indicative features. They can be useful in determining the climatic, physical, and chemical conditions of sedimentation and stratigraphic constructions, and in clarifying the geological development history of the studied region.

The Cretaceous period in the history of the Earth is interesting not only from the point of view of global events occurring during this time but also in terms of the huge mineral reserves concentrated in the deposits synchronous with it. In the Far East Region, Cretaceous rocks occupy a significant part of the territory. Hundreds of papers have been written on the geology, stratigraphy, and mineral resources of this area. However, mineralogically, the rocks of this period are less characterized, especially from an authigenesis point of view. There are only separate works [1–3] on some regions of the Russian Far East. The purpose of this work is to summarize the mineralogical studies carried out by the author on the Cretaceous rocks of this area.

2. Methods

Rock samples collected from the abovementioned area were mainly studied using X-ray diffraction, as well as electron and optical microscopy, thermography, and chemical analyses as additional tests. The phase structures of the clay and non-clay minerals were determined from bulk rock cement. The samples were crushed in an agate mortar and sieved to a size less than 0.06 mm. The resulting fractions were prepared in an aqueous suspension and applied to a glass slide for orientation. They were analyzed under different conditions [4,5]: air drying, glycol saturation, and heating for three hours at 550 °C. Some minerals selected under a binocular microscope were prepared with alcohol and analyzed in powder. On a fraction smaller than 1 μm, which was obtained from some samples by gravity sedimentation [4], a silicate wet chemistry analysis with atomic absorption ending on AA-6800 (Shimadzu, Japan) was carried out. The following tools were used: a "Dron-2.0" diffractometer (NPO "Burevestnik", Russia) with Cu Kα radiation (flat graphite monochromator), an anode voltage of 40 kV, and a current of 30 mA; an optical polarizing microscope, "Amplival" (Carl Zeiss Jena); and a derivatograph, "Q-1000" (Paulik, MOM, Budapest, Hungary). Electron microscopy and optical microscopy were applied for layered silicate morphology, microstructure determination, preliminary descriptions, and mineral formation staging. The determination of mixed-layer formations was carried out according to [4–7].

3. Material

The material for this study was sampled from Cretaceous volcanogenic–sedimentary rocks (Figures 1–6, Figure S1 [8], Table S1), obtained by the author on field trips to the Primorye Region during coastal expeditions to the Sakhalin (the Terpeniya Peninsula) and Shikotan islands in 2000–2009. It was obtained via dredging in the Sea of Japan (the Yamato Upland) and the Kuril Island Arc (the Underwater Vityaz Ridge), and data on the Kamchatka Peninsula (western part, the Palana Section) were obtained. During the coastal trips, mainly coarse-grained rocks (sandstones, tuff sandstones, and the cement of gravelites and conglomerates) were selected with a sampling frequency of 10–50 m in normal layering and without visible traces of alterations. Sometimes, fine-grained rocks were studied. Each sample dredged from underwater uplands was also analyzed. Using an X-ray analysis, the author personally analyzed over 1200 samples of Cretaceous rocks from the Primorye Region (≈900), the Yamato Upland (Sea of Japan, ≈50), the Terpeniya Peninsula (Sakhalin Island, ≈20), Shikotan Islands (Lesser Kuril Arc, ≈200), the Underwater Vityaz Ridge (≈50), and the Palana Section (Western Kamchatka, 10).

The main parts of the samples were taken from the Cretaceous volcanogenic–sedimentary rocks of the southern and partially central parts of Primorye. The data were published in [9,10]. New data are presented in Figure 1, Figure S1, and Table S1. These data regard the Lower Cretaceous rocks of the Taukhinskaya (Berriasian–Early Valanginian), Klyuchevskaya (Valanginian), Ust-Kolumbinskaya (Hauterivian), Kemskaya (Aptian–Middle Albian), Divninskaya (Early Albian), Svetlovodnenskaya (Early–Middle Albian) Suites, Nikanskaya (Barremian–Middle Albian), the Suchanskaya (Hauterivian–Albian) series, the Middle and Upper Cretaceous formations of the Korkinskaya (Late Albian–Early Cenomanian), and Primorskaya (Turonian (Santonian)–Campanian?) series, covering the period from the Berriasian to the Campanian [11]. In the Sea of Japan, Early Cretaceous (Albian) rocks have only been found on the Yamato Upland [12,13] (North and South Yamato Ridges, Figure 2). The Cretaceous rocks of the Terpeniya Peninsula (Sakhalin Island) [14,15] are represented by volcanic–siliceous rocks of the Uchirskaya Suite (Maastrichtian–Danian, Kotikovskaya Series, Figure 3). On Shikotan Island (Figure 4), the Cretaceous [16,17] rocks of the Krabozavodskaya (Albian–Campanian), Matakotanskaya (Campanian–Maastrichtian), and Malokuril'skaya (Maastrichtian–Danian) Suites are considered. The volcanogenic–sedimentary rocks of the Underwater Vityaz Ridge (region of the Kuril Island Arc) exposed in some places (presumably of Late Cretaceous–Maastrichtian–Danian age) (Figure 5) are partially represented in [18,19]. The rocks of the Palana District (Campanian–Maastrichtian age, Western Kamchatka, Figure 6) [20] and the rocks of the Il'pinsky Peninsula (Eastern Kamchatka, the Unal'skaya Suite, presumably of Late Cretaceous age) are described in [1–3].

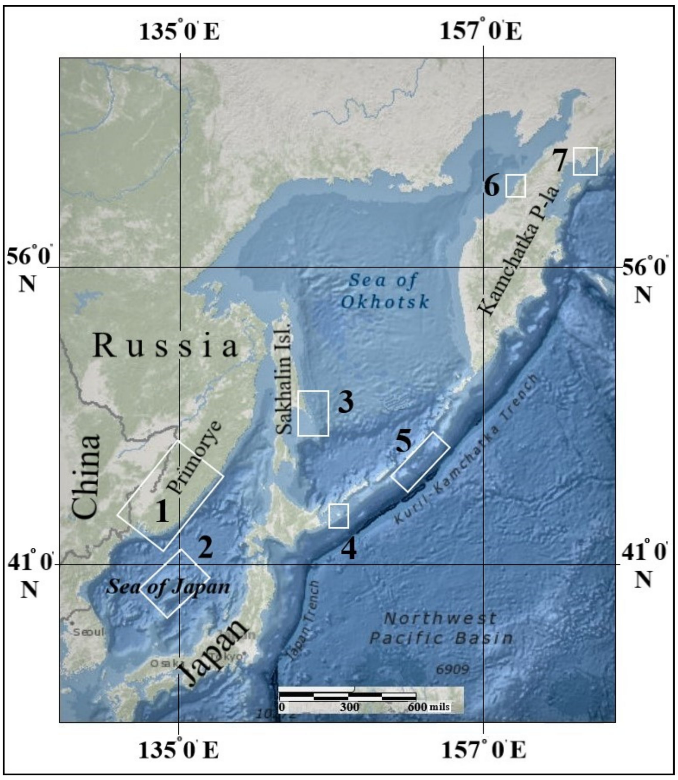

Figure 1. Simplified map of the studied area. 1—Primorye Region, 2—Yamato Upland, 3—Terpeniya Peninsula, 4—Shikotan Island, 5—Underwater Vityaz Ridge, 6—Palana District, 7—Il'pinsky Peninsula.

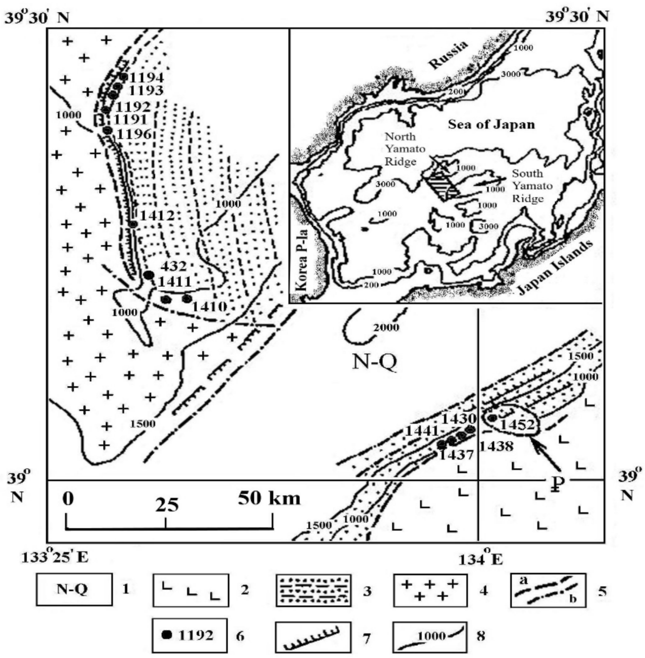

Figure 2. Geological chart of the Yamato Upland (Sea of Japan) [12,13]. Location of corrensite-bearing rocks. 1—marine Neogene-Quaternary deposits; 2—Cenozoic volcanic rocks (basalts, andesites and their tuffs); 3—Early Cretaceous rocks; 4—Late Paleozoic rocks (granits, diorites and gneisses); 5—geological boundaries: a—assumed, b—established; 6—dredging stations; 7—tectonic faults; 8—isobaths (m); (₽) Paleocene rocks.

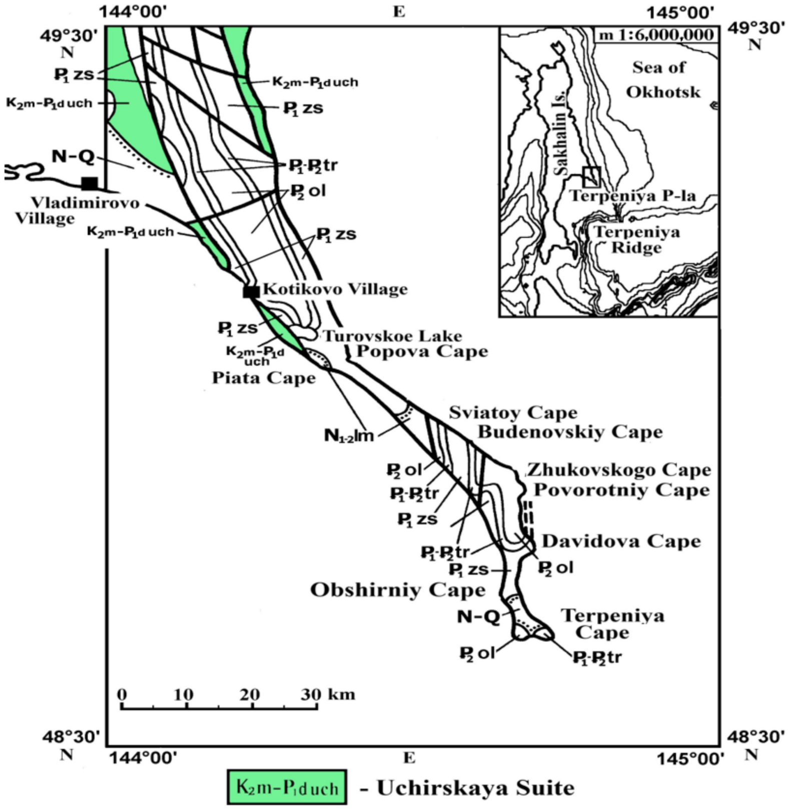

Figure 3. Geological chart of the Terpeniya Peninsula (Sakhalin Island) [14,15].

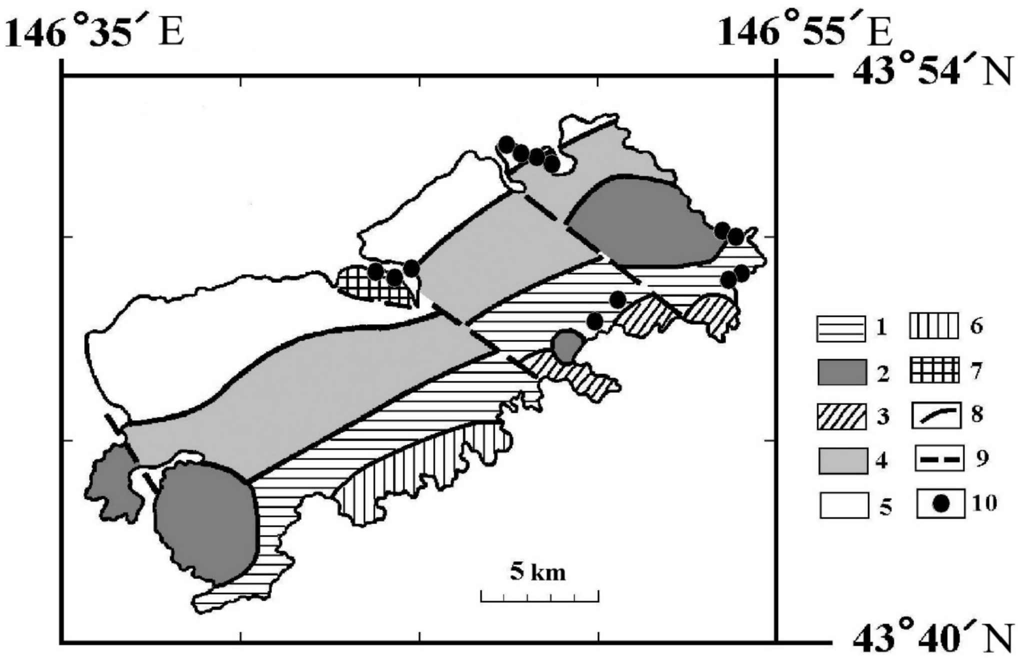

Figure 4. Geological chart of the Shikotan Island (Kuril Arc System) (according to [16,17]; with minor changes). 1—Zelenovskaya Suite, 2—intrusive complex of Shikotan gabbroids, 3—Dimitrovsky complex (basalts, andesite-basalts, diabases, dolerites) of parallel dikes; 4—Malokuril'skaya Suite, 5—Matakotanskaya Suite; 6—Malokuril'skiy igneous complex (basalts, shoshonites), 7—Krabozavodskaya Suite, of pillow-basalts; 8—geological boundaries; 9—faults; 10—sampling points.

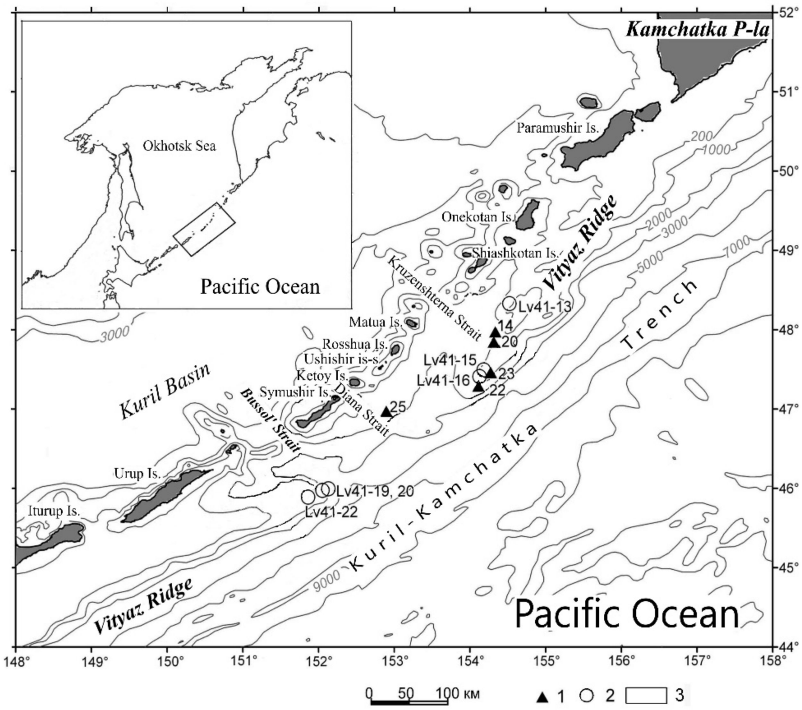

Figure 5. Location of dredging stations for the R/V Akademik M.A. Lavrentiev" [18,19]. 1—stations of the 37th cruise, 2—stations of the 41st cruises, 3—studied area.

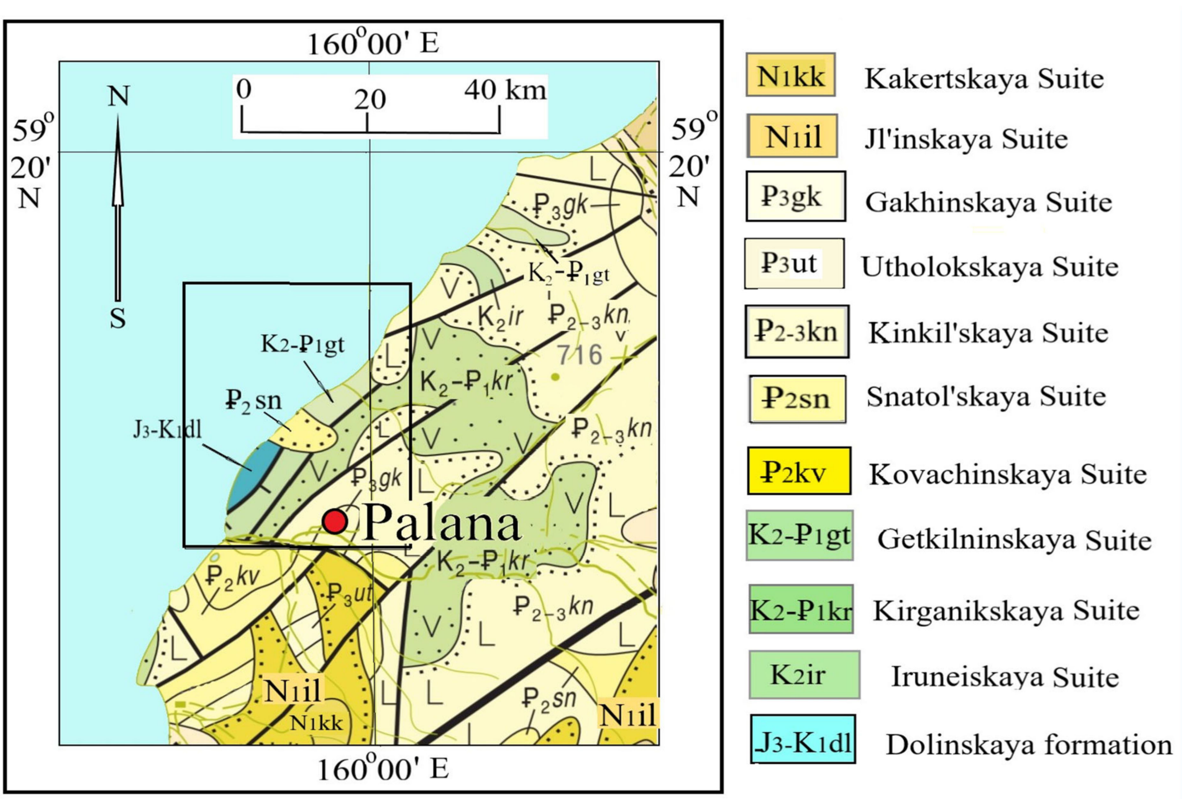

Figure 6. Palansky Section studied area, Western Kamchatka [8,20].

4. Results

Clay and non-clay minerals in volcanogenic–sedimentary rock cement have previously been studied in detail: along the Southern Primorye [9,10,21], the Yamato Upland [22], the

Terpeniya Peninsula (Sakhalin Island) [15,23], the Shikotan Island [23], and Vityaz Ridge (Kuril Arc) [23,24] (Figures 1–6, Figure S1, and Table S1 [25,26]).

Clay minerals developed in the Cretaceous volcanogenic–sedimentary rock cement of the northeastern part of the transition zone from the Asian continent to the Pacific Ocean are represented by chlorite, illite, swelling chlorite, vermiculite (?), kaolinite, smectite (?), corrensite, mixed-layer chlorite–smectite, rectorite, and mixed-layer illite–smectite varieties. Non-clay minerals are calcite, ankerite, epsomite, tschermigite, gypsum [27], barite [28], zeolites (laumontite, analcime, and stilbite), cristobalite, goethite, quartz, and plagioclase (Figures S2–S8 [25,26,29]). Smectite and mixed-layer formations of the smectite–illite type (low-ordered, R0) are very rare in Cretaceous rocks. Mixed-layer illite–smectite (highly ordered structures, R1) appears at the turn of the Paleogene and Cretaceous, as well as regular mixed-layer chlorite–smectite (corrensite) ones. Cristobalite is occasionally found in the rocks of the Maastrichtian–Danian (Uchirskaya Suite, the Terpeniya Peninsula) and earlier periods. Kaolinite is only found in the Triassic and Lower and Upper Cretaceous rocks of Primorye, and on the Yamato Upland (Sea of Japan). The sulfate group of minerals (epsomite, gypsum, barite, tschermigite, and ankerite) is only present in the Lower Cretaceous rocks of the Yamato Upland (Sea of Japan). Zeolites: laumontite is found in the Cretaceous and Paleogene rocks of Primorye and the Lower Cretaceous rocks of the Yamato Upland; analcime and stilbite predominantly developed in both sedimentary and volcanogenic–sedimentary rocks of the Lower and Upper Cretaceous. Carbonates: calcite is very common in Cretaceous rocks in the forms of veins and veinlets, and ankerite (possibly redeposited, slightly rounded) is only found on the Yamato Upland (Sea of Japan).

The mineral associations found in the Cretaceous rock cement of Southern Primorye are chlorite–illite (illite–chlorite), corrensite–chlorite, chlorite–corrensite–mixed-layer chlorite–smectite–laumontite, illite–rectorite–mixed-layer illite–smectite, and illite–kaolinite–quartz. The Yamato Upland (Sea of Japan) is characterized by the above associations, but the mineral composition is much richer. The composition of the mineral associations in other studied areas is somewhat poorer. No illite–kaolinite–quartz (no kaolinite) association is found. A chlorite–corrensite–mixed-layer chlorite–smectite association is rare, and laumontite is absent (not determined?), but other zeolites are present.

5. Discussion

Before beginning, it is necessary to agree on the terminology and nature of the minerals found in the cement of the studied rocks.

Corrensite is a 1:1 regular interstratification (50/50) of trioctahedral chlorite with a trioctahedral smectite (low charge). It has 29 A in air-dried and 32 A in glycosylated conditions and an integer series of reflections. All other differences similar in diffraction pattern, which have a shoulder in the small angle area, and different orders of layering and composition were called mixed-layer chlorite–smectite minerals [4,5,27,30–32] or corrensite-like minerals [6,7,33]. Rectorite is a 1:1 regular interstratification (50/50) of dioctahedral mica and dioctahedral smectite. It has 26 A in air-dried and 29 A in glycosylated conditions and an integer series of reflections. All other differences similar in diffraction pattern (similar to that mentioned above) were called mixed-layer illite–smectite minerals [4,5,27,30–32] or rectorite-like minerals [6,7,33]. Mixed-layer illite–smectite minerals interlayered with different degrees of ordering (R0) were also distinguished. Chlorite and kaolinite were separated by the presence of 14.4, 7.2, 4.8, 3.59 and 3.53 A reflections, which did not change after glycosylation; 7.2 and 3.59 A for kaolinite and 14.4, 7.2, 4.8 and 3.53 A reflections for chlorite; accordingly, Mica has 10.0, 5.0, and 3.34 A reflections, which did not change after glycosylation [4,5]. Chlorite, kaolinite, corrensite, rectorite, and other mixed-layer formations are not recognized under light microscopy.

As for the nature (authigenic or detrital) of clay minerals, the author accepts the statement that most of the rock cement is authigenic, as it is believed that a fraction of less than 0.06 mm is represented mainly by this and only an insignificant part of it can be involved in the grinding from clasts [4,34–36]. As a rule, these are quartz and plagioclase.

This statement is partially confirmed by viewing thin sections, where it can clearly be seen that corrensite, kaolinite, illite, and quartz are authigenic (Figure S8a–c). In the case of mica (illite), this is also confirmed by electron microscopic studies (Figure S8d), as well as the diffraction patterns of samples of various ages. In modern sediments, we observe sharp, high, symmetrical peaks of detrital mica and chlorite. With the aging of sedimentary rocks, the peak belonging to smectite (001) begins to increase in intensity and narrows. The peaks of terrigenous mica and chlorite decrease significantly. Highly ordered mixed-layer illite–smectite and chlorite–smectite formation types begin to appear in the cement of Oligocene rocks. Corrensite and rectorite are maximally developed in Paleogene and Upper Cretaceous rocks. In the Lower Cretaceous rocks, we observe the presence of chlorite in association with corrensite and laumontite, and illite. In the rocks of the Jurassic and older, we still mainly find the illite–chlorite association.

Some non-clay minerals are also authigenic. These are laumontite (Figures S7 and S8b), sometimes quartz (Figure S8c), epsomite, tschermigite, barite (Figure S7), cristobalite, and calcite. Ankerite may be terrigenous. In thin sections, it looks slightly rounded. This is also the case for analcime in the Lower Cretaceous rocks of the Yamato Upland, which is represented by formations that look similar to ooids or peas, as if impregnated in the rock. In other areas, analcime can develop over pyroclastic fragments. This is also the case for other zeolites, which are widely represented in Upper Cretaceous rocks.

Therefore, we can confidently consider corrensite, rectorite, laumontite, illite, epsomite (interlayer in siltstone), tschermigite, barite (crusts on slip mirrors), sometimes quartz (Figure S8c), and cristobalite (interlayer in radiolarite) as authigenic. As conditionally authigenic, we can take chlorite, calcite, sometimes ankerite, and analcime. The remaining minerals can be considered detrital. Therefore, the main emphasis in our discussion focuses on the confidently authigenic minerals. However, nature (origin) is not so important from the author's point of view. The appearance of minerals in rocks of the same age from different regions is much more important.

The most representative results of the mineralogical analysis were obtained for the Lower Cretaceous rocks of South Primorye [9,10]. The samples from the Upper Cretaceous rocks of Primorye (Primorskaya Series) are much less characterized. The new data (Table S1) did not change the previously obtained conclusions. In the Upper Cretaceous rocks, there is a tendency for the predominance of the illite–chlorite association, the greater presence of mixed-layer chlorite–smectite and mixed-layer illite–smectite, illite, swelling chlorite (?), and stilbite. There is a decrease in the content of corrensite and rectorite. Kaolinite is absent.

All other studied areas with Upper Cretaceous rocks, such as the Terpeniya Peninsula [15,23], Shikotan Island [23], the Underwater Vityaz Ridge [23,24], Western (Palansky Section) (Table S1), and Eastern Kamchatka [1–3], with rare exceptions, are mineralogically similar to those described above. The Upper Cretaceous rocks of the Primorye Region, the Terpeniya Peninsula (Uchirskaya Suite, Maastrichtian–Danian), and on Shikotan Island, in addition to the above corrensite, mixed-layer chlorite–smectite, rectorite, mixed-layer illite–smectite, analcime, and stilbite, appear (Table S1).

In the distribution of minerals and mineral associations in the cement of the studied Cretaceous rocks, latitudinal, age, and chemical zonation are observed. The southern (a) and northern (b) zones can be distinguished as follows: (a) characterized by the presence of kaolinite and minerals of the sulfate group in the Lower Cretaceous rocks of the Yamato Upland (Sea of Japan), possibly the Primorye Region, and a weak magnesian content of mixed-layer chlorite–smectite formations (Tables 1 and 2) [1,2,25,26,37], and (b) distinguished by the absence of minerals of the sulfate group and kaolinite, and a slightly increased magnesian content of mixed-layer chlorite–smectite varieties. Age zoning is expressed as follows: in the Lower Cretaceous rocks, chlorite–corrensite and chlorite–corrensite–laumontite associations dominate; in the Upper Cretaceous rocks, the role of the mixed-layer chlorite–smectite and mixed-layer illite–smectite formations with the appearance of analcime and stilbite is increased.

Table 1. The average chemical composition of mixed-layer chlorite–smectite minerals and corrensites of different genetic groups (fractions less than 1 μm).

Components	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	(*n* = 4)	(*n* = 4)	(*n* = 2)	(*n* = 2)	(*n* = 6)	(*n* = 2)	(*n* = 3)	(*n* = 3)	(*n* = 1)	(*n* = 3)	(*n* = 3)	(*n* = 6)	(*n* = 7)	(*n* = 10)	(*n* = 3)	(*n* = 3)	(*n* = 6)	(*n* = 6)	(*n* = 6)
FeO	13.92	15.62	10.27	11.03	14.66	11.2	11.7	9.77	9.8	15.47	17.03	10.27	19.44	9.94	3.88	0.88	6.21	15.50	12.03
MgO	6.24	5.44	2.09	5.06	9.23	1.74	1.23	3.52	1.90	5.55	9.69	16.03	10.47	20.77	23.47	2.78	1.90	7.16	3.65
CaO	0.14	0.09	1.78	0.77	1.02	0.94	0.06	1.26	3.77	1.17	1.13	1.70	2.08	1.67	1.43	0.36	0.35	3.27	1.63
Na_2O	1.51	1.61	1.04	1.15	1.01	2.56	1.55	2.54	2.48	1.90	1.60	0.35	1.11	0.51	0.12	0.36	1.09	1.33	1.01
K_2O	1.90	2.55	4.17	2.74	1.81	3.16	3.57	2.54	0.93	1.90	1.60	2.62	0.95	0.33	0.64	0.09	5.14	1.24	2.02

Note. Mixed-layer chlorite–smectite minerals: 1, from Lower Cretaceous sandstones and aleuroargillites of the Southern Yamato Ridge; 2, from Paleocene sandstones and aleuroargillites of the Southern Yamato Ridge; 3, from volcanogenic–sedimentary rocks of Shikotan Island; 4, from volcanogenic–sedimentary rocks of the Terpeniya Peninsula; 5, from volcanogenic–sedimentary rocks of the Vityaz Ridge; 6, from Paleogene volcanogenic–sedimentary rock (southern Primorye Region): of the Kraskinskaya; 7, Khasanskaya; 8, Nazimovskaya Suite; 9, from Lower Cretaceous volcanogenic–sedimentary rocks (southern Primorye Region) of the Korkinskaya Series; 10, Galenkovskaya; 11, Lipovetskaya suites. Corrensites: 12, from terrigenous-carbonate-evaporitic formations; 13, from the deep epigenesis zone of the clastic- and volcanogenic formations; 14, from hydrothermally altered basic and ultra-basic rocks; 15, from carbonate-dolomite formations; 16, from hydrothermally recycled gypsum–dolomite rocks (12; 15; and 16, I genetic type; 13, II; 14, III) [37]; 17, fraction less than 1 μm from Lower Cretaceous sandstones of the Sikhote Alin; 18, from Paleogene sandstones of the Il'pinsky and 19, Kronotsky peninsulas (Kamchatka) [1,2].

Table 2. Chemical composition and formula of the <1 μm fraction from Cretaceous volcanogenic–sedimentary rocks of some districts of the Far East Region.

Components	Southern Primorye								Underwater Vityaz Ridge		
in wt%	Chl-Sme			Crr					Chl-Sme	Crr	
No	4	18	84	85	128	176	178	181	LV-41-19-1p	LV-41-16	LV-41-15-8
SiO_2	52.3	53.8	53.8	42.6	43.3	41.1	41	40.3	47.02	38.47	39.98
Al_2O_3	19.6	16.9	19.4	17	17.8	17.9	15.4	17.2	18.47	15.57	13.64
Fe_2O_3 tot	11.7	9.8	9.4	19.2	17.8	18.2	15.9	17	10.5	19.55	18.09
TiO_2	0.83	0.87	0.8	0.71	0.81	0.52	0.91	0.68	1.5	0.36	0.14
MnO	0.08	0.16	0.15	0.15	0.18	0.07	0.11	0.07	0.05	0.182	0.062
MgO	2.56	1.9	2.43	7.32	6.91	8.76	10.93	9.37	3.43	14.64	15.28
CaO	0.11	3.77	1.07	0.91	1.54	0.83	1.6	0.97	1.21	0.25	0.14
Na_2O	1.08	2.48	1.65	2.01	2.05	1.29	2.07	1.43	0.92	1.19	0.66
K_2O	3.75	0.93	1.65	2.01	2.05	1.29	2.07	1.43	1.96	0.44	0.53
LOI	6.62	8.47	7.44	9.09	9	8.77	8.68	11.14	14.96	10.05	11.66
∑summ	98.63	99.08	97.79	101	101.4	98.73	98.67	99.59	100.02	100.702	100.182
Si	3.57	3.70	3.67	3.06	3.08	2.99	3.01	2.98	3.46	2.81	2.96
Al	1.58	1.37	1.56	1.44	1.49	1.53	1.33	1.50	1.60	1.34	1.19
Fe	0.60	0.51	0.48	1.04	0.95	1.00	0.88	0.95	0.58	1.07	1.01
Ti	0.04	0.05	0.04	0.04	0.04	0.03	0.05	0.04	0.08	0.02	0.01
Mn	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.00
Mg	0.26	0.19	0.25	0.78	0.73	0.95	1.20	1.03	0.38	1.59	1.69
Ca	0.01	0.28	0.08	0.07	0.12	0.06	0.13	0.08	0.10	0.02	0.01
Na	0.14	0.33	0.22	0.28	0.28	0.18	0.29	0.21	0.13	0.17	0.09
K	0.33	0.08	0.14	0.18	0.19	0.12	0.19	0.14	0.18	0.04	0.05

Note: 4—Lower Cretaceous, Ust-Kolumbiyskaya Suite; 18—Lower-Upper Cretaceous, Korkinskaya Suite (Luk'yanovka); 84, 85, and 128—Lower Cretaceous, Nikanskaya Series, Galenkovskaya Suite? (De-Friz Peninsula); 176, 178, and 181—Lower Cretaceous, Nikanskaya Series, Lipovetskaya Suite (t. Vladivostok, Klykova Cape) [9]; LV-41-19-1p and LV-41-16—Upper Cretaceous, Underwater Vityaz Ridge. Chl-Sme—mixed-layer chlorite–smectite; Crr—corrensites [25,26].

The main conclusions made earlier [9] are that the chlorite–illite (illite–chlorite) association is found in all formations and that it cannot be determinative by itself. For the kaolinite–illite association, the time of formation can be established as Aptian–the beginning of the Early Albian—113–120 Ma (coal accumulation, the "Lipovetskoe" period, is noted in the Lipovetskaya Suite, Suchanskaya Series, and North Yamato Ridge). For the corrensite–chlorite association, it is the beginning of the Early Albian—110–113 Ma (noted in the Lipovetskaya and Galenkovskaya Suites, and Suchanskaya and Korkinskaya series); for the corrensite–chlorite–laumontite association, it is the second half of the Albian—105–110 Ma (the “Galenkovskoe” period, which is recorded in the Galenkovskaya Suite, Suchanskaya and Korkinskaya series, and South Yamato Ridge); and for rectorite, it is the Late Cenomanian—93–95 Ma (the “Korkinskoe” period, reddish color sediments of the Korkinskaya Series (Romanovskaya Suite)).

Therefore, within the “Lipovetskoe” period, we have two events: one for the kaolinite–illite association, 113–120 Ma (coal accumulation epoch), and one for the corrensite–chlorite association, 110–113 Ma; this period is comparable to the Early Albian event (Paquier event, OAE 1b, 111 Ma). For the “Galenkovskoe” period (the presence of laumontite), the interval can be defined as 105–110 Ma. The nearest global events with a marked supply of calcium in sedimentary deposits are recorded at the boundaries of 103, 105, and 107.5 Ma, corresponding to Urbino, OAE1c, and OAE1d, respectively. Such a multiplicity can be explained by the repetition of events increasing calcium supply to the sea basin, i.e., there may be several supply periods, and they may not yet have been sufficiently studied in these deposits.

The formation interval of the reddish colored sediments of the Korkinskaya Series (upper part of the Romanovskaya Suite) is 93–95 Ma (the epoch of lateritic weathering), which coincides in time with the Cenomanian–Turonian events (OAEs—Bonarelli event, C/T OAE, OAE2, ~93 Ma).

In general, the proposed scheme of mineral formation for the Cretaceous rocks of Southern Primorye [9] does not undergo any special changes. Therefore, it becomes possible to extend the information obtained to areas with a lesser degree of knowledge.

The new data obtained make it possible to identify at least two more periods in the Upper Cretaceous stage of sedimentation, probably associated with the existence of conditions favorable for the evaporation of seawater (corrensite association). In the Primorskaya (mainly volcanic) Series, corrensite is found in sandstones in the areas of Zalesye Village [9] and Dal’negorsk area (Table S1). The problem of sandstones in that strata is debatable. Both olistostromal and normally sedimentary origins are possible. Consequently, the deposits of this period (Santonian–Campanian, 72–83 Ma) require more detailed studies.

In the rocks of the Maastrichtian–Danian period, another event appears, which is recorded in almost all Upper Cretaceous rocks (Table S1). Corrensite, mixed-layer chlorite–smectite and rectorite, and mixed-layer illite–smectite encountered the most likely fall on the sediments bordering on the Upper Cretaceous deposits. These are the Uchirskaya (Terpeniya Peninsula and Sakhalin Island) and Malokuril’skaya (Shikotan Island) Suites, and basement rocks on the Vityaz Ridge (Maastrichtian–Danian, 61–72 Ma). It is possible that the pyrite of the black shales found on Shikotan Island reflect an OAE1d event (Campanian–Maastrichtian).

These include coastal marine conditions, some with the possible evaporation of sea water, and others under conditions of adjacent chemical weathering. Detailed locations and descriptions of these deposits are given in [9] (Figure S2).

The latest data [38] for the south of Primorye Region give two absolute ages for the Early Cretaceous period of coal accumulation—118 $\pm$ 1.4 and 109 $\pm$ 1 Ma for the Lipovetskaya (Nikanskaya Series) and Frentsevskaya (Suchanskaya Series) Suites, respectively. Now, it is possible to specify the time of existence of the kaolinite–illite association (the period of coal accumulation or the first “Lipovetskoe” event); the time is older than 118 $\pm$ 1.4 million years and in the region of 109 million years. P.V. Markevich [3] notes the appearance of kaolinite in the section of the Cretaceous rocks of Primorye in three periods—Barremian–Aptian, Aptian–Albian, and the end of the Albian (129–125, 125–113, and 100 Ma, respectively). Chlorite prevails in the interval of 113–100 Ma, which coincides with the periods and conditions of sedimentation identified by the author [9]. The chlorite–corrensite suites in this study are confined to Cretaceous sedimentation periods between

119 and 109 Ma, whereas the other identified mineral suites range in age between 129 and 100 Ma.

The presence of chlorite–corrensite and chlorite–corrensite–laumontite associations, which can manifest themselves in two stages, can be correlated with several periods: (1) the chlorite–corrensite association, younger than 118 $\pm$ 1.4 Ma, and the second "Lipovetskoe" event, 113–115 million years, and (2) the chlorite–corrensite–laumontite association, younger than 109 $\pm$ 1 million years, the "Galenkovskoe" period (event) (probable analog of the Frentsevskaya Suite and Suchanskaya Series).

A special role should be assigned to the corrensite–laumontite association. The corrensites found in the Cretaceous rocks of the studied region (Table 2) are similar in chemical composition to the Fe–Mg–corrensite minerals of the Cretaceous coal-bearing formation of Western Verkhoyansk [33]. Such an association of corrensite–laumontite is fairly well characterized in [39–41]. It is widely believed that laumontite is a function of depth and temperature, while corrensite is formed due to the femic components of volcanic–sedimentary material with intermediate and basic compositions. The author suggests a different nature of this association in which smectite (sepiolite and palygorskite?) is formed under conditions close to evaporitic conditions (seawater evaporation), and laumontite (or some other zeolite) with an increased content of calcium in sandy sediments is formed after smectite (fills the pores later), with both of them, smectite and zeolite, being transformed during epigenesis into corrensite and laumontite. Calcium carbonate can form concretions (boudins) and secondary fissured veinlets common in Cretaceous rocks. In these cases, the relevance of finding calcite together with laumontite and corrensite should be studied more carefully. In the Primorye Region, corrensite in association with laumontite is found at least in the Lower Cretaceous and Paleogene–Neogene rocks. In the Upper Cretaceous rocks, the zeolites of stilbite and heulandite types predominantly develop, which is also noted in [33] for the coal-bearing formation of the Western Verkhoyansk Region. Therefore, a similar regularity can be found in other sedimentary coal-bearing basins of the Far East.

It should be assumed that some of the Lower Cretaceous rocks of the Yamato Upland (Sea of Japan) may also have similar stages in sedimentation since similar mineral associations have been identified there (Table S1).

Some rock samples of the North Yamato Ridge are probably from approximately 118 $\pm$ 1.4 Ma (kaolinite–illite association) and possibly a little younger (113–115 Ma, due to the presence of corrensite and mixed-layer chlorite–smectite varieties). The age of some samples of the Southern Yamato Ridge can vary from 118 $\pm$ 1.4 to 109 $\pm$ 1 Ma (due to the presence of kaolinite and corrensite with laumontite, respectively). The presence of epsomite, barite, ankerite, and analcime, and the signs of brine evolution in silty mudstones [22] indicate that the conditions for the evaporation of seawater in the Early Cretaceous in the area of the Yamato Upland were more pronounced than in Primorsky sedimentary basins. It is possible that, in the Late Cretaceous, the area of the Yamato Upland could serve as a zone for the supply of sedimentary material to the regions of Southern Primorye for deposits similar to the upper parts of the Korkinskaya Series (Cenomanian?). Some samples of stations 1410b and 1411 (Table S1) are massive goethite, which could be formed during lateritic weathering or under an oxygen-rich environment [42]. It is true that no similar specimens have been found in the Southern Primorye to date.

6. Conclusions

When analyzing the clay mineral assemblages of Cretaceous rock cement in the transition zone from the Asian continent to the Pacific Ocean, the following six periods in sedimentation are distinguished, possibly associated with world global climatic events: 113–120, 110–113, 105–110, 93–95, 72–83, and 61–72 Ma. The first three periods are confirmed by absolute data [38], but the others require clarification.

According to M.A. Levitan et al. [43], during the Cretaceous, up to six or more temperature maxima could be observed, during which salt-bearing deposits could form under the conditions of seawater evaporation.

The conclusion is confirmed that, for the Lower and Upper Cretaceous rocks of this region, analcime or laumontite facies of epigenesis are possible [44]. During epigenesis, two parallel processes are observed: (1) the progressive transformation of smectite into mica under "oxidizing" (environment saturated with oxygen) [45] conditions in the presence of potassium and (2) chloritization under the condition of an excess of calcium and magnesium under "reducing" (oxygen deficiency) conditions, i.e., the transformation of smectite into mica reflects the course of epigenetic processes, while the transformation into corrensite reflects the specific conditions of sedimentation for a given region [33,46,47]. It should be noted that, in the direction from south to north, the magnesian content of corrensite increases (Table 1), which may indicate a meridional orientation of the salinization process.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12070909/s1, Table S1: Clay and non-clay minerals in Cretaceous rocks cement of the studied area; Figure S1: Geological map of the central part of Primorye Region; Figure S2: Oriented X-ray diffraction patterns of the main associations of clay and non-clay minerals in the Lower Cretaceous sedimentary rocks cement; Figure S3: Oriented X-ray diffraction patterns of clay and non-clay minerals in the Lower Cretaceous sedimentary rocks cement of the Northern Yamato Ridge; Figure S4: Oriented X-ray diffraction patterns of clay and non-clay minerals in the Lower Cretaceous sedimentary rocks cement of the Northern Yamato Ridge; Figure S5: Oriented X-ray diffraction patterns and thermograms of mixed-layer chlorite-smectite minerals in the Lower Cretaceous sedimentary rocks of the Southern Yamato Ridge; Figure S6: Oriented X-ray diffraction pattern of the Upper Cretaceous sedimentary rocks cement of Palana Section (Western Kamchatka, sample 87d); Figure S7: Powder X-ray diffraction patterns of minerals in the Lower Cretaceous sedimentary rocks of the Southern Yamato Ridge; Figure S8: Images from polarizing optical and electron-microscope of the well-sorted Lower Cretaceous sandstones of the Yamato Upland.

Funding: This work was supported by the Ministry of Science and Education of Russia (project 121021700342-9).

Data Availability Statement: The data presented in this study are available on request from the author.

Acknowledgments: The author expresses his deep gratitude to T.N. Palechek for the materials provided on the Cretaceous rocks of the Palana Section (Western Kamchatka).

Conflicts of Interest: The author declares no conflict of interest.

References

1. Chudaev, O.V. Distribution of clay minerals in flysch deposits of Eastern Kamchatka. *Lithol. Miner. Resour.* **1978**, *1*, 105–115. (In Russian)
2. Markevich, P.V.; Chudaev, O.V. Composition of flish Sikhote-Alin and Kamchatka sandstands and paleotectonic conditions of its formation. *Dokl. Acad. Sci. USSR* **1979**, *246*, 428–431. (In Russian)
3. Markevich, P. *Geosynclinal Terrigenous Sedimentation in Eastern Asia in the Phanerozoic on the Example of Sikhote-Alin and Kamchatka*; Nauka: Moscow, Russia, 1985; p. 117. (In Russian)
4. Brindley, G.W.; Brown, G. (Eds.) *Crystal Structures of Clay Minerals and Their X-ray Identification*; Miner. Soc.: London, UK, 1980; p. 495.
5. Moore, D.M.; Reynolds, R.C. *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, 2nd ed.; Oxford University Press: New York, NY, USA, 1997; p. 400.
6. Drits, V.A.; Sakharov, B.A. X-ray structural analysis of mixed-layer minerals. In *Tr. GIN*; Nauka: Moscow, Russia, 1976; Volume 295, p. 256. (In Russian)
7. Drits, V.A. Mixed-layer minerals: Diffraction methods and structural features. In Proceedings of the International Clay Conference, Denver, CO, USA, 28 July–2 August 1985; Schultz, L.G., van Olphen, H., Mampton, F.A., Eds.; Clay Miner. Soc.: Bloomington, IN, USA, 1987; pp. 33–45.
8. Gusev, N. *State Geological Map of the Russian Federation. Scale 1: 1,000,000*, 3rd ed.; Far Eastern Series; VSEGEI: St. Petersburg, Russia, 2011. (In Russian)
9. Mozherovsky, A.V. Practical Application of the Mineralogical Mapping Method for Stratigraphy of the Cretaceous Deposits of Southern Primorye (Russian Far East). *Minerals* **2021**, *11*, 840. [CrossRef]
10. Mozherovsky, A.V. Authigenic minerals of paleozoic-cenozoic volcanogenic-sedimentary rocks in the Southern Primorye Region. *Russ. J. Pac. Geol.* **2021**, *15*, 583–601. [CrossRef]

11. Syasko, A.; Vrzhosek, A.; Dubinsky, A.; Kononets, S.; Korotkiy, A.; Kutub-Zade, T.; Lyakh, I.; Nevolin, P.; Popov, V.; Rodionov, A.; et al. *State Geological Map of the Russian Federation, Scale 1: 200,000. Sikhote-Alinskaya Series. Sheets K-52-XII, XVIII*; Explanatory Letter; Moscow Branch of FSBI VSEGEI: Moscow, Russia, 2016; p. 241. (In Russian)
12. Lelikov, E.P.; Markevich, V.S.; Terekhov, E.P. Lower Cretaceous and Paleogene deposits of the Yamato Upland (Sea of Japan). *Dokl. Acad. Sci. USSR* **1980**, *253*, 678–681. (In Russian)
13. Bersenev, I.I.; Lelikov, E.P.; Bezverkhny, V.L.; Vashchenkova, N.G.; S'edin, V.T.; Terekhov, E.P.; Tsoy, I.B. *Geology of the Sea of Japan Bottom*; Far Eastern Branch of the USSR Academy of Sciences: Vladivostok, Russia, 1987; p. 140. (In Russian)
14. Tsoy, I.B.; Terekhov, E.P.; Shastina, V.V.; Gorovaya, M.T.; Mozherovskii, A.V. Age of the Kotikovaya group in the Terpeniya Peninsula (Eastern Sakhalin). *Stratigr. Geol. Correl.* **2005**, *6*, 632–643.
15. Terekhov, E.P.; Mozherovsky, A.V.; Gorovaya, M.T.; Tsoy, I.B.; Vashchenkova, N.G. Composition of the rocks of the Kotikovo group and the main stages in the late cretaceous-paleogene evolution of the Terpeniya Peninsula, Sakhalin Island. *Russ. J. Pac. Geol.* **2010**, *3*, 260–273. [CrossRef]
16. Govorov, G.I. Geodynamics of Small-Kuril Paleoarc system after geochronological and petrochemical data. *Dokl. Earth Sci.* **2000**, *4*, 521–524. (In Russian)
17. Govorov, G.I. *Phanerozoic Magmatic Belts and Origin of the Okhotsk Sea Geoblock Structure*; Dalnauka: Vladivostok, Russia, 2002; p. 198. (In Russian)
18. Kulinich, R.G.; Karp, B.Y.; Lelikov, E.P.; Karnaukh, V.N.; Valitov, M.G.; Nikolaev, S.M.; Kolpashchikova, T.N.; Tsoi, I.B.; Baranov, B.V. Structural and Geological Characteristics of a «Seismic Gap» in the central part of the Kuril Island Arc. *Russ. J. Pac. Geol.* **2007**, *1*, 3–14. [CrossRef]
19. Lelikov, E.P.; Tsoy, I.B.; Emel'yanova, T.A.; Terekhov, E.P.; Vashchenkova, N.G.; Vagina, N.K.; Smirnova, O.L.; Khudik, V.D. Geological Structure of the Submarine Vityaz Ridge within the Seismic Gap Area (Pacific Slope of the Kurile Island Arc). *Russ. J. Pac. Geol.* **2008**, *2*, 99–109. [CrossRef]
20. Palechek, T.N.; Solov'ev, A.V.; Shapiro, M.N. Structure and age of Mesozoic sedimentary-volcanogenic deposits of the Palana Section (Western Kamchatka). *Stratigr. Geol. Correl.* **2003**, *11*, 261–277.
21. Mozherovsky, A.V. Geology and stratigraphy of the Posiet Peninsula (South Primorye) from a mineralogical point of view. *Bull. Kamchatka Reg. Assoc. Educ. Sci. Cent. Earth Sci.* **2019**, *3*, 26–37. (In Russian)
22. Mozherovsky, A.V.; Terekhov, E.P. Authigenic minerals in Early Cretaceous and Paleocene sedimentary rocks of the Yamato Ridge, East Sea. *Geosci. J.* **1998**, *2*, 148–159. [CrossRef]
23. Mozherovsky, A.V.; Terekhov, E.P. Authigenic minerals of Meso-Cenozoic volcanic-sedimentary rocks of marginal seas bottom of the North-Western Pacific. *Stand. Glob. J. Geol. Explor. Res.* **2016**, *3*, 105–114.
24. Terekhov, E.P.; Mozherovsky, A.V.; Tsoy, I.B.; Lelikov, E.P.; Vashchenkova, N.G.; Gorovaya, M.T. Late Mesozoic and Cenozoic volcanosedimentary complexes from the submarine Vityaz Ridge, the Island Arc slope of the Kuril-Kamchatka Trench, and its evolution. *Russ. J. Pac. Geol.* **2012**, *3*, 209–216. [CrossRef]
25. Warr, L.N. Recommended abbreviations for the names of clay minerals and associated phases. *Clay Miner.* **2020**, *55*, 261–264. [CrossRef]
26. Warr, L.N. IMA–CNMNC approved mineral symbols. *Mineral. Mag.* **2021**, *85*, 291–320. [CrossRef]
27. Terekhov, E.P.; Mozherovsky, A.V.; Vashchenkova, N.G.; Barinov, N.N. Authigenic gypsum mineralization in the bottom rocks of the Sea of Japan and Okhotsk. *New Data Miner.* **2013**, *48*, 62–69. (In Russian)
28. Terekhov, E.P.; Mozherovsky, A.V.; Barinov, N.N. Barites from the underwater Yamano Ridge (Japan Sea). *Stand. Glob. J. Geol. Explor. Res.* **2016**, *4*, 161–169.
29. MacKenzie, R.C. (Ed.) *Differential Thermal Analysis. Volume 1: Fundamental Aspects*, 1st ed.; Academic Press: London, UK; New York, NY, USA, 1970; p. 804.
30. Cuadros, J.; Fiore, S.; Huertas, F.J. Introduction to Mixed-Layer Clay Minerals. In *Interstratified Clay Minerals: Origin, Characterization and Geochemical Significance*; AIPEA Educational Series, Pub. No. 1; Fiore, S., Cuadros, J., Huertas, F.J., Eds.; Digilabs: Bari, Italy, 2010; p. 175.
31. Guggenheim, S.; Adams, J.M.; Bain, D.C.; Bergaya, F.; Brigatti, M.F.; Drits, V.A.; Formoso, M.L.L.; Galán, E.; Kogure, T.; Stanjek, H. Summary of recommendations of nomenclature committees relevant to clay mineralogy: Report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2006. *Clay Miner.* **2006**, *41*, 863–877. [CrossRef]
32. Guggenheim, S. Introduction to Mg-rich clay minerals: Structure and composition. In *Magnesian Clays: Characterization, Origin and Applications*; AIPEA Educational Series, Pub. No. 2; Pozo, M., Galán, E., Eds.; Digilabs: Bari, Italy, 2015; pp. 1–62.
33. Drits, V.A.; Kossowskaya, A.G. *Clay Minerals: Smectites, Mixed-Layer Silicates*; Nauka: Moscow, Russia, 1990; p. 214. (In Russian)
34. Gibbs, R.J. Clay mineral segregation in the marine environment. *J. Sediment. Petrol.* **1977**, *47*, 237–243. [CrossRef]
35. Pettijohn, F.J.; Potter, P.E.; Siever, R. *Sand and Sandstone*; Springer: New York, NY, USA; Berlin/Heidelberg, Germany, 1973; p. 644.
36. Konta, Y. Phyllosilicates in the sediment-forming processes: Weathering, erosion, transportation, and deposition. *Acta Geodyn. Geomater.* **2009**, *6*, 13–43.
37. Kossovskaya, A.G. Genetic types and paragenetic association of minerals of the corrensite groupe. In Proceedings of the International Clay Conference, Madrid, Spain, 23–30 June 1972; Serratosa, J.M., Sanchez, A., Eds.; Division de Ciencias, C.S.I.C.: Madrid, Spain, 1973; Volume 1, pp. 341–342.

38. Golovneva, L.; Bugdaeva, E.; Volynets, E.; Sun, Y.; Zolina, A. Angiosperm diversification in the Early Cretaceous of Primorye, Far East of Russia. *Foss. Impr.* **2021**, *2*, 231–255. [CrossRef]
39. Iijima, A.; Utada, M. Present-day zeolitic diagenesis of the Neogene geosynclinal deposites in the Niigata oil field Japan. In *Molecular Sieve Zeolites-I, Advances in Chemistry Series, 101*; Flanigen, M., Sand, L.B., Eds.; American Chemical Society: Washington, DC, USA, 1971; pp. 342–349.
40. Kimbara, K.; Sudo, T. Chloritic clay minerals in tuffa-ceous sandstones of the miocene Green Tuff Formation Yamata district, Ishicava Perfecture, Japan. *J. Jpn. Assoc. Mineral. Petrol. Econ. Geol.* **1973**, *68*, 246–258. [CrossRef]
41. Mehegan, J.M.; Robinson, P.T.; Delaney, J.R. Secondary mineralization and hydrothermal alteration in the Reydarfjordur drill core, Eastern Iceland. *J. Geophys. Res. Solid Earth* **1982**, *87*, 6511–6524. [CrossRef]
42. Liu, X.; Hu, X.; Li, J. Cretaceous oceanic anoxic and oxic events. *Chin. J. Nat.* **2020**, *4*, 347–354, (In Chinese with English Abstract).
43. Levitan, M.A.; Antonova, T.A.; Gelvi, T.N. Mesozoic-Cenozoic sedimentation in the Circum-Arctic Belt. 2. Cretaceous-Paleogene. *Geochem. Int.* **2015**, *5*, 411–429. [CrossRef]
44. Aoyagy, K.; Kazama, T. Transformational changes of clay minerals, zeolites and silica minerals during diagenesis. *Sedimentology* **1980**, *27*, 179–188. [CrossRef]
45. Kossovskaya, A.G.; Drits, V.A. Problems of crystal chemical and genetic classification of micaceous minerals of sedimentary rocks. In *Epigenesis and Its Mineral Indicators*; Nauka: Moscow, Russia, 1971; pp. 71–95. (In Russian)
46. Hauff, P.L. Corrensite: Mineralogical Ambiguities and Geologic Significance. In *Open-File Report 81-850*; United States Department of the Interior Geological Survey: Washington, DC, USA, 1981; p. 45.
47. Hazen, R.M.; Sverjensky, D.A.; Azzolini, D.; Bish, D.L.; Elmor, S.C.; Hinnov, L.; Milliken, R.E. Clay mineral evolution. *Am. Mineral.* **2013**, *98*, 2007–2029. [CrossRef]