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CALCITE PSEUDOMORPHS (PSEUDOGAYLUSSITE, JARROWITE, THINOLITE, GLENDONITE, GENNOISHI, WHITE SEA HORNLETS) IN SEDIMENTARY ROCKS. ORIGINS OF THE PSEUDOMORPHS

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The paper discusses the geographical locations, the tectonic, stratigraphic, and facial correlations, relationships with the country rocks, internal structure, and mineral and chemical composition of calcite pseudomorphs. Their presence in sedimentary rocks is usually a paleoclimatic indicator of low temperatures during the sediment formation.

Approximately 150 years ago calcite pseudomorphs after an unknown mineral were first found in recent silts of the White Sea and the alluvial Quaternary sediments in Thuringia. At the present time these rare formations have been described in sedimentary rocks from various parts of the world under different names (barley corns, pseudogaylussite, jarrowite, thinolite, glendonite, White Sea hornlets, and gennoishi).

The perfect edges, unusual for sedimentary rocks, and the giant size of a great number of the pseudomorphs have attracted attention of numerous workers, including Blum, Des Cloiseau, J. and E. Dana, Eremeev, and others. In the "System of Mineralogy" (J. Dana et al. 1953) a special chapter deals with pseudomorphs. However, the identity of the original mineral remains unclear.

There is more than just mineralogical aspect to the problem as pseudomorphs occur in a wide stratigraphic range from the Carboniferous to the Quaternary in North America, Europe, Asia, Australia and are certain to be an index of specific paleogeographic settings in which sediments were formed.

Over the years of study, the original mineral — later replaced by calcite or, in rare cases, other new formations — was supposed to be gaylussite, glauberite, gypsum, celestine, anhydrite, sulfur, thenardite, and rhombal carbonate. In the majority of studies the identifications were based on crystallographic measurements. However, the diversity of the preceding list is in itself evidence that the purely geometric method is inadequate for determining the genesis of the pseudomorphs and additional geological and geochemical data are necessary.

The present paper makes exactly this kind of attempt of a comprehensive approach to pseudomorphs as it investigates the geological settings of formation of pseudomorphs, general features of their composition and structure, and the probable nature of the original mineral. A survey of the main deposits of pseudomorphs has been given elsewhere (Kaplan 1979),* where the reader can find a catalog of the sites, all chemical analyses available, and a complete bibliography.

Most of the samples in the collection studied here were from the Jurassic and the lower Cretaceous of Eastern Siberia (collection of Kaplan supplemented with samples of Meledina, Nal'nyaeva, Kirina, and Zharkov). Single pseudomorphs from the Upper Permian at the Mezen River (Tatarskii's collection), the Tertiary of Western and Northern Kamchatka (collections of Suzdal'skii, the Leningrad University, and the Mineralogical Museum of the Academy of

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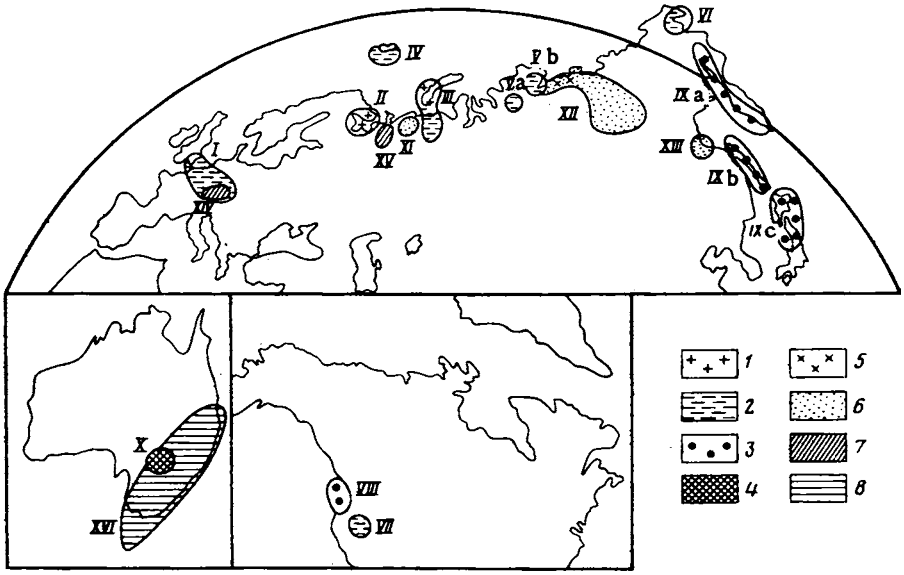

Fig. 1. Occurrence of pseudomorphs. Sediment: 1) Recent; 2) Quaternary; 3) Paleogene and Neogene; 4) upper Cretaceous; 5) lower Cretaceous; 6) Jurassic; 7) Permian; 8) Permian-Carboniferous. I) Western Europe (Britain, West Germany, East Germany, Holland, Hungary); II) White Sea; III) Polar Urals (Pai-Khoi) and Nova Zemlia; IV) Spitsbergen; V) Taimyr; Va) Pyasina River basin; Vb) Bolshaya Balakhnya River Basin; VI) Chukotka; VII) Great Basin Plateau (Lahontan Lake); VIII) Washington and Oregon states; IXa) Koryak Upland and Western Kamchatka; IXb) Sakhalin; IXc) Japan (Hokkaido and Honshu); X) Australia (White Cliffs); XI) Timan-Pechora Region; XII) northwestern Siberia (Eastern Taimyr, and Khatanga, Anabar, Olenek, Lena, and Indigirka river basins; XIII) Okhotsk Sea shore; XIV) East Germany (Thuringia); XV) Mezen River basin; XVI) Australia (Queensland, New South Wales, Tasmania).

Sciences of the USSR), the Recent sediments of the White Sea (collections of the Leningrad Mining Institute and the Mineralogical Museum of the Academy of Sciences of the USSR), and the Quaternary of East Germany (collections of the Freiburg Mining Academy* and the Mineralogical Prospecting Institute), were also investigated.

Occurrence of Pseudomorphs

Geographical Locations. Pseudomorphs are mainly found in the Northern Hemisphere in various parts of Europe, Asia, and North America (Fig. 1, Table 1). Most deposits are concentrated north of 60°N and just a few are situated south of it, between 40 and 60°N. In the Southern Hemisphere pseudomorphs have been found in Australia south of 20-25°S. Paleomagnetically adjusted latitudes (Table 1) taken from the maps of Smith et al. (1973) vary visibly for the Permian and Triassic (?) of Europe and North America, shifting towards lower latitude (10-30°N), and the Permian-Carboniferous and Upper Cretaceous of Australia, which shift towards higher latitudes (50-70°S).

Tectonic Correlations. Sediments containing pseudomorphs were formed in diverse platform and geosynclinal settings. In the eugeosynclines Meso-Cenozoic sediments of the Pacific belt were accumulated, and, in the miogeosynclines, the Jurassic strata of the Verkhoyan-Kolyma folded country and the Permian-Carboniferous of Australia. All other pseudomorph deposits are situated on platforms.

There is no clear confinement of pseudomorphs to smaller structural units. Studies of various Jurassic and lower Cretaceous sections covering a major portion of northern East Siberia show that pseudomorphs are widespread on the platform and folded sides of the Mesozoic troughs in various elements of the synclinal and anticlinal structures of different orders.

*Material obtained by courtesy of R. Starke.

Stratigraphic Occurrence. Pseudomorphs occur in Permian—Carboniferous, Permain, Jurassic, Cretaceous, Paleogenic, Neogenic, Quaternary, and Recent sediments. Pseudomorph-type formations have been found in the Triassic as well. The major deposits are confined to the Permian—Carboniferous (Lower Permian?) Bajocian—Bathian, Oligocene—Miocenic, and Quaternary strata.

Layers containing pseudomorphs are consistent both horizontally and vertically. In the Jurassic of East Siberia that has been studied in detail (zone by zone) pseudomorph horizons are traceable for 1000-2000 km. The constant morphological features of pseudomorph crystal growths make it possible to use them for a bed by bed correlation of distant sections.

Facies Confinement. Pseudomorphs were formed in a wide spectrum of facial settings — continental alluvial and lacustrine, deltal and lagoonal, and shallow and deep sea (see Table 1). The peak in pseudomorph abundance is confined to shallow sea (sublittoral) deposits. The greatest variety of facial types is characteristic of the Quaternary. This may be a sign of incomplete geological record since sea shelf sediments are the best preserved fossils.

Depths at which pseudomorph-containing sediments were formed varied from tens of meters (alluvial settings) to 200 m (lacustrine* and sublittoral sea settings) to several hundred and probably more meters (deep sea). Water salinity varied from several tenths of 1% (alluvial, lacustrine settings) to 3.6% (deltal, marine desalted and normal saline basins); pH varied from slightly alkaline in sea basins to slightly acid in alluvial (flood plain?) conditions. Eh at the sediment surface for continental and marine settings (judging by the presence of burrowing organisms) were positive. In the deepsea conditions of the Oligocenic—Miocenic Pacific basin, according to the presence of taxodonts, some oxygen deficit might have existed in bottom water.

Temperatures at which pseudomorph-containing sediments were formed are also essential. For major pseudomorph deposits in the Permian—Carboniferous of the Southern Hemisphere and in the Quaternary and Recent rocks of the Northern Hemisphere they correlate directly with major glaciations. These deposits in North America, Eurasia, and Australia lie near medium and high paleolatitudes (40-80°) and are within the occurrence zone of ice sheets.

Quaternary pseudomorphs in Europe occur together with skeletal remains of the mammoth and cave bear (van Calker 1897). The Chukotka pseudomorphs of the same age and the Permian—Carboniferous pseudomorphs of Australia are confined to ice-sea sediments (Petrov 1966; David et al. 1909). The pseudomorphs of the Quaternary Lahontan Lake in the United States were formed in a period when the lake level lowered, apparently due to the dry climate of the glacial epoch. The pseudomorph-bearing beds of the Lahontan Lake contain no remains of sweetwater organisms which are typical of the surrounding lacustrine limestone (Russel 1885). Low water temperatures might have been responsible for the disappearance of gastropods and fish at the time when the pseudomorph beds were formed. At high latitudes (60-65°) a part of Paleogenic—Neogenic (Kamchatka), Jurassic, lower Cretaceous (Canada), and Upper Createaceous (Australia) deposits are located. The latter, too, could have been found during glaciation. The rest of the Tertiary, Jurassic, and Cretaceous deposits occur north of 35-40°N. In the recent cold climatic epoch these are areas of moderate, subarctic, and arctic climate. Milder conditions apparently prevailed there during the Paleogene, Neogene, Jurassic, and Cretaceous. Yet pseudomorph occurrence in the Jurassic and Neogene clearly correlates with periods of colder climate. The coolings are indicated by megaclasts appearing scattered in the pseudomorph strata below the Lower and Middle Jurassic of Siberia (Kaplan 1976), faunal features — a uniform set of sthenothermal belemnites in the Bajocian and Bathonian of North Siberia (Saks and Nal'nyaeva 1976), abundance of cold water yoldia in the upper Oligocene and Miocene of the Pacific region (Gladenkov 1970), poor maturity of clay sediments and a low content of labile lattice minerals in them observed in the North Siberian Jurassic (Kaplan 1976), and lowered mean annual temperatures. These temperatures, estimated by geochemical data (Ca, Mg, Sr, O^{18}/O^{16} in belemnite rostra) and pelecipods, are 7-16°C for the main Paleogenic—Neogenic and Bajocian—Bathonian deposits (Saks and Nal'nyaeva 1975; Durham 1959). Taking into account seasonal fluctuations, temperature lowering with depth (particularly for the deepsea Pacific finds), and the likelihood of

*The maximum depth of the Quaternary Lake Lahontan in North America at the stage of pseudomorph formation was 150 m (Russel 1885).

TABLE 1. Occurrence of Pseudomorphs

Facial type	Geological age	Paleo-latitudes	Country rocks	Local name	Deposit	Probable original mineral*
Alluvial	Quaternary	50-54° N	Loam	Pseudogaylusseite, barley-corn, Gerstenkörner, jarrowite	Britain (Durham), Holland (Dollart, Onderdendam), East Germany (Sanderhausen, Kating)	Gaylussite (Breithaupt, 1836; Rose, 1841; Geinitz, 1876); celestine (von Rath, 1868; Des Cloiseoux, 1874; Miers, 1897; Trenchmann, 1902); gypsum (Des Cloiseoux, 1843); anhydrite (Groth, 1878); unclear (van Calker, 1897)
Deltaic	Same	71-73° N	Sand—silt and clay	—	Taimyr (Agapa and Bolshaya Balakhna rivers)	Calcite (Suzdal'skii, 1968); gypsum (Brodskaya and Kengarten, 1975)
Lacustrine	Same	40-50° N	Limestone	Thinolite (U.S.A.)	Hungary, U.S.A. (Lahontan Lake)	Gaylussite (Haidinger, 1841; King, 1878); $CaCO_3$; $CaCl_2$ or $CaCO_3$; $2NaCO_3$ (Dana, 1885)
Lagoonal (high salinity)	Upper Permian	10-30° N	Limestone	—	Germany (Thuringia), Western Europe (Mezen)	Gaylussite (Schmid, 1880; Plotnikov and Tatarskii, 1946); gypsum (Plotnikov, 1964)
Shallow marine	Recent	64-67° N	?	White Sea hornlets	White Sea	Celestine (Eremeev, 1882)
Same	Quaternary	65° N	Loam	—	Chukotka	Calcite (Petrov, 1965, 1966); gypsum (Brodskaya and Rengarten, 1975); gaylussite (Hiki, 1897, 1915)
Same	Paleogene and Neogene	36-63° N	Silt—clay	Gennoishi	Northern and Western Kamchatka, Sakhalin, Hokkaido, Honshu; U.S.A. (Oregon and Washington)	Thenardite (Jkegami, 1965, 1967, 1969); gypsum (Brodkskaya and Rengarten, 1975); gypsum (Jaquet, 1892; Pelican, 1900); sulfur (Weisbach, 1898)
Same	Upper Cretaceous	65°S	Same	Pipe-apple	Australia	Glauberite (Anderson, Jevons, 1905); gpysum or unknown easily soluble salt (Gürich, 1901)
Same	Lower Cretaceous	48-52° N	Silt—clayey, rarely fine-grained sandstone	—	Northern part of Eastern Siberia (Eastern Taimyr, and basins of the rivers Khatanga, Anabar, Olenek, and the lower reaches of Lena)	Glauberite (Eremeev, 1887)

Same	Same	52° N	Silt–clay	—	Spitsbergen	Calcite (Pchelina, 1965)
Same	Same	60-70° N	Same	Hedgehogs	Canada (Sverdrup basin)	Thenardite (Kemper, Schmitz, 1976)
Same	Jurassic	55-65° N	Silt–clayey, rarely fine-grained sand stone	—	Eastern Siberia (Western Yakutia, northern Krasnoyarsk Province)	—
Same	Permian–Carboniferous	50-70° N	Silt–clay	glendonite	Eastern Australia	Glauberite (David et al., 1909; Carne, 1909; Woolnough, 1910; Twelvetrees, 1912; Walkom, 1913; Brown, 1925; Whithouse, 1933; Raggatt, 1938)
Deepsea	Paleogene and Neogene	50-65° N	Same	—	Western Kamchatka, Sakhalin	Gypsum (Brodskaya and Rengarten, 1975)

*For a complete list of references to this column see M. E. Kalan, manuscript deposited at VINITI, April 24, 1979, No. 1471-79 Dep.

abnormal minima, it seems realistic to assume that temperature dropped down to zero centigrade at the time when pseudomorph-bearing strata were formed.

The confinement of pseudomorphs to humid cold zone is not observed for data on the Permian and Triassic deposits, which occur between 10 and 30°N. These finds are mainly confined to motley (red) formation and the carbonate facies of zechstein that formed in the conditions of hot and contrastive (variably humid) climate. The probability of sharp temperature drops is not great even though at present short spans of frost and snow are observed at 30°N (Gulf of Mexico). It should be noted that the Permian pseudomorphs have peculiar traits (Fig. 2 (5)) that distinguish them drastically from the morphological type of all other deposits.

Generally, the facies conditions of pseudomorph formation appear as the sublittoral cold water sea basin of a normal or slightly lowered salinity. The probable physicochemical characteristics of the bottom water are: pH $\approx$ 7-8, +Eh, t $\sim$ 0 — +5-10°C (?). In conjunction with the decomposition of organic matter, slightly acid—slightly reducing conditions might have prevailed in the sediment. The facial variety of pseudomorph-containing deposits shows frequent considerable deviations from this "average" setting. Temperature is the most stable parameter, viz., solution temperature close to 0°C.

Distribution by Rock Type. Pseudomorphs have been found in limestone, calcitic and dolomitic marls, and clayey, silty, and sandy rocks (see Table 1). Most pseudomorphs occur in silty and sandy rocks — siltstone, clayey siltstone, less often silty clays and argillites. A small number have been found in calcitic and dolomitic marls (Permian), limestone (lacustrine Quaternary), and sandy rocks (Jurassic and lower Cretaceous).

Pseudomorphs are frequently found inside carbonate nodules and nodule lenses, sometimes inside pyrite concretions (Fig. 3 (6), (7)), but all such enclosing rocks are of a diagenetic origin.

The general composition of pseudomorph-containing rocks is diverse. Detailed studies have been carried out of the Jurassic and Cretaceous of northern East Siberia, containing numerous pseudomorphs consisting of lithoclasts, arkoses, and multicomponent (chloritic—hydromicaceous with kaolinite, smectite, and mixed-layer minerals) clay rocks (Kaplan 1976).

Pseudomorph Occurrence. Most typical is an unordered distribution in the country rock, particularly in the case of larger crystals up to tens of centimeters long and radial crystal growths. While larger crystals pierce the layers, smaller crystals in radial growths are enveloped by them.

Frequently, pseudomorphs occur perpendicularly to the layering. These are usually growths of smaller crystals which, like the associated carbonate and pyrite tubular concretions, developed in burrows. Sometimes single crystals or growths of 2-3 crystals are positioned parallel to the layering, which is typical of the pseudomorphs associating with vegetable remains (Taimyr Quaternary) and found in thin clay rock interlayers amid sands (Chukotka Quaternary).

The amount of pseudomorphs varies in a wide range — from several to hundreds per 1 m^3 of rock. Maximum contents are typical of spherical growths of small crystals, while minimal concentrations are observed for giant sword-shaped formations.

Generally, data on the pattern of occurrence of pseudomorphs — envelopment inside the layers, confinement to burrows, and presence of large (up to 80 cm and more) crystals radially oriented from a common center in different directions — are indications that the crystals were growing in liquid ooze near the water-sediment contact. This is corroborated by the layering contiguous to some crystals and the presence of rounded, ferruginated growths apparently washed out of sediment and redeposited (marine sediments of North Siberian Jurassic).

Internal Structure and Composition of Pseudomorphs

These features of pseudomorphs exhibit a striking ubiquitous similarity, according to data from thin sections of pseudomorphs from Recent sediments of the White Sea, Quaternary of England, Holland, Germany, Taimyr, Chukotka, and the U.S.A., the Paleogene and Neogene of Kamchatka, Hokkaido, northwestern United States, the lower Cretaceous and Jurassic of northern Siberia, the Permian—Carboniferous of Australia, as well as chemical analyses of pseudomorphs from various deposits.

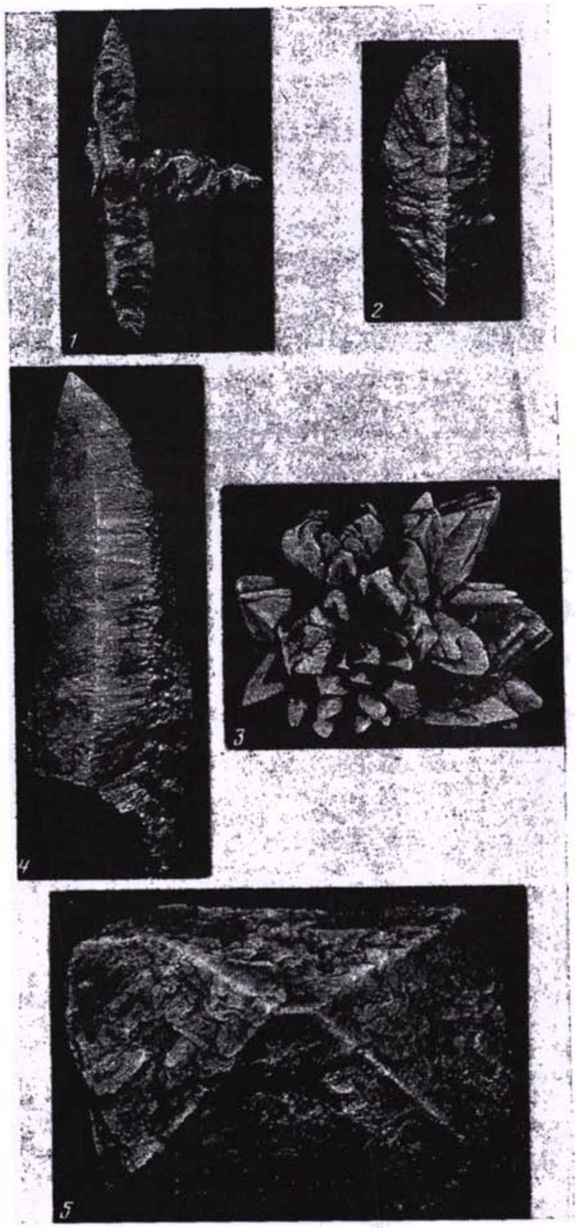

Fig. 2. Typical forms of pseudomorphs from different sites. 1) Recent White Sea deposits, gray pseudomorph. Reduction ×2 (White Sea hornlet, Leningrad Mining Institute); 2) Quaternary, Sangerhausen (East Germany), white. Magnified ×2 (barley corns, pseudogaylussite, Freiburg Mining Academy); 3) Quaternary (Pleistocene) of Bolshaya Balakhna basin (Eastern Taimyr), spherical growth, white. Splitting of larger crystals can be seen. Reduced ×2 (Leningrad University); 4) Jurassic (Bajocian) of the Nordvik Bay shore (northern East Siberia), brown, oil-soaked pseudomorph. Reduced ×1.5; 5) Upper Permian of the Mezen basin (northeastern European part of Russia). Gray sample. Reduced ×2 (V. B. Tatarskii).

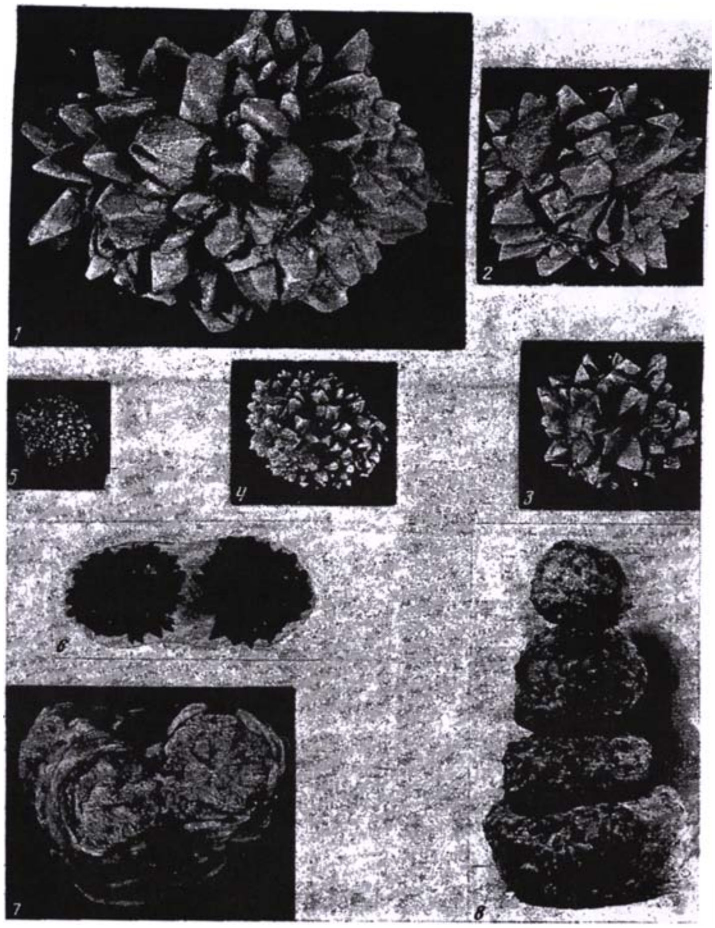

Fig. 3. Typical growths of pseudomorph crystals from Jurassic (Bajocian and Bathian) of the Anabar Bay coast (northern East Siberia). 1-5) Stellate spherical light-gray growths of various sizes. Flattenings along the stratification and less developed crystals at the bottom of the growths are typical. Reduced ×2; 6) two small spherical, brown stellate growths flattened along the stratification inside a carbonaceous nodule. Concentric position of the areas of secondary calcite (white) and zonal coloring by bitumen (dark perimeter) are seen. Ground-in, actual size; 7) two small white stellate growths inside pyrite nodule. Reduced ×1.5; 8) pyramid of spherical and flattened growths of dark brown crystals cemented by dark gray clay—carbonaceous matter. Reduced ×2.

Pseudomorph Structure. Pseudomorphs consist of an aggregate of differently colored calcite grains. The coloring varies from nearly white and yellowish to yellow in light-colored country rocks to gray, dark-gray with a brown shade, and red-brown in the dark clay rocks and nodular interbeds to brown in oil-permeated pseudomorphs. Many crystals and growths have a characteristic zonal coloring which is dark on the perimeter and lighter towards the center (Fig. 3 (6)). In the Jurassic pseudomorphs of Siberia a direct correlation is observed between C_{org} content and the color intensity — light-gray and gray differences contain 0.15-1.18%, dark red 0.31-0.45% of C_{org}. A great number of Recent and Quaternary pseudomorphs in Europe, Asia, North America and the Jurassic pseudomorphs of Eastern Siberia have a friable porous structure. Inside they are sugary and grainy with a dense shell that usually has an opaque or shiny surface. This structure is common for pseudomorphs from friable slit—sand rocks and lacustrine carbonate sediments less affected by catagenesis. The least-altered Quaternary pseudomorphs from the Lahontan Lake typically contain, in square cross sections, concentric edges and, in rectangular sections, sometimes an additional longitudinal edge.

The longitudinal cut shows edges converging toward one crystal end at an average angle of 35°. When pseudomorphs are filled with secondary calcite the details of inner structure become less distinct (Dana 1885). A concentric zonal structure is also observed in the cross section of pseudogaylussites of Sangerhausen (Geinitz 1876), jarrowites from the Clyde River (Trenchmann 1902), and the Aalenian pseudomorphs from Taimyr.

The more altered pseudomorphs from other deposits usually exhibit a more monolithic build. Depending on the structure, their density varies in a wide range from 1.9 g/cm^3 for friable samples to 2.65 g/cm^3 for dense varieties, with porosity ranging, accordingly, from 20-25 and more to 2%. Normally, the pseudomorphs are denser than the enclosing rocks.

The surface of pseudomorphs, particularly of the light-colored varieties, is often motley, due to the presence of idiomorphous elongated and wedgelike gray calcite grains with a glassy luster, 1-1.5 mm long, mainly oriented along the crystal axis and sometimes merged into schlieren-type areas of up to 1 × 2 cm. The grains are cemented by a predominantly basal lamellar chinalike calcitic mass which is of a lower hardness, lighter color, and better solubility in hydrochloric acid. Pores, fissures, and interstices between the crystals in the growths and their central parts are frequently filled with milk-white calcite.

In the microscope three consecutive calcite generations are seen. The first is represented by calcite grains: large (up to 3 mm) with inclusions of fine (0.001-0.003 mm) clay-organic particles positioned concentrically parallel to the grain contour; large pure grains; small (0.05-0.2 mm) isometric grains with various amounts of clay-organic flakes admixed to them. The grain facets are straight or curved and the contour is tabular in the cross section and rounded in the longitudinal section in relation to the pseudomorph axis, with the predominant elongation and optical orientation being parallel to the axis or the facets of the pseudomorph. The second generation is fine-grained, sometimes radial, spherulitic, columnar calcite filling interstices between the grains and sometimes forming columnar crusts on the pseudomorph facets. The quantity of second-generation calcite varies in a wide range from 10 to 30-40%. The last generation is big calcite crystals in pores and fissures (Fig. 4). Usually it amounts to a few percent, at most 10-25% in rare cases. This generation is colorless unlike the preceding two, which are often colored, by unequally oxidized bitumoid, in different shades of yellow. The clay-organic particles tinge the grains with gray; in reflected light they appear cotton white.

In the least-altered pseudomorphs from the Lahontan Quaternary limestone, the first-generation calcite constitutes the internal edges while the interstices are filled with the second-generation calcite.

In the Tertiary and Quaternary pseudomorphs of the Far East and Taimyr, Brodskaya and Rengarten (1975) have registered traces of algal structure. They believe that all the pseudomorphs were formed after a skeleton of algal threads composed of monocrystalline calcite which included bands of brown organic material. However, neither we, nor the algologists M. B. Gnilovskaya, N. I. Strel'nikova, and A. G. Voitsekhovskaya, who have kindly examined our collection, were able to find traces of algae in any of the 50 samples under study. It is possible that the algal threads observed by Brodskaya and Rengarten (1975) were an accessory organogenic component of the pseudomorphs like the remains of wood, pelecipods, brachiopods, and corals found in some pseudomorphs from the Quaternary of Chukotka and Taimyr and the Permian-Carboniferous of Australia.

Mineral composition of pseudomorphs is remarkably uniform. The principal component is calcite, which, according to chemical analysis and x-ray data, frequently contains 5-6 mol. % $MgCO_3$ and $FeCO_3$. Reports of the presence of aragonite (Dana 1885; Eremeev 1882; Brodskaya and Rengarten 1975; and others) and siderite (Brown 1925) have not been confirmed by optical and x-ray data. However, the Upper Cretaceous pseudomorphs of Australia consist of opal instead of calcite. One Australian specimen was pure gypsum (David et al. 1909). Beside calcite, pseudomorphs consist of a minor amount of clastic and clay particles trapped from the country rocks and also newly formed pyrite, gypsum, barite, kaolinite, chalcedony, and opal, which fill pores and fissures and form films and crusts on the surface of the pseudomorphs.

Fig. 4. Inner structure of a spherical growth of small crystals from the Bajocian of the Anabar Bay shore (northern East Siberia). White areas are coarse-grained secondary calcite; dark areas, calcite grains enriched in fine clay-organic particles; gray background, calcite grains colored with light-yellow bitumen. Top left shows split corroded crystals. Thin section, crossed nicols, ×15.

Average chemical composition of pseudomorphs is tabulated in Table 2. The main component is carbonate calcite (87.62%). The insoluble residue, R_2O_3, and other components never exceed 2.5%. Sesquioxides of C_{org}, partly Fe_2+Mg, P are largely linked with the non-carbonate component of pseudomorphs. A small quantity of SO_3 (up to 0.48%) reflects the presence of some gypsum and sometimes barite. Spectral analysis of Jurassic pseudomorphs of northern Siberia determined minor Cr, Ti, Cu, Zr, and Ca, which, too, belong to the insoluble residue. The carbonate constituent of pseudomorphs is as follows (wt. %): $CaCO_3$ 94.54, $FeCO_3$ 2.26, $MgCO_3$ 2.57, $MnCO_3$ 0.39, $SrCO_3$ 0.21. The Ba content, according to spectral data, is 0.001-0.028%. According to x-ray data these elements replace Ca in the calcite lattice.

Two features of the pseudomorph composition are noteworthy: absence of Mg at low concentrations of Mn, Fe, and Sr in some crystals and heightened organic content. The average C_{org} composition in pseudomorphs is 0.44% but in the insoluble residue the share of organics is 19% and sometimes as high as 50% or more. This indicates that fine opaque particles scattered inside calcite grains are organic or clay-organic material.

Microprobe investigation of North American Tertiary pseudomorphs (Boggs 1972) showed an increased content of isomorphous Mg and Fe from first generation (large tabular rounded grains) towards the second and third generation (spherulites and mosaic calcite in pores and fissures). In the first, second, and third calcite generation, respectively, the following quantities were found (%): CaO 54.34-53.44-53.61, MgO 0.54-0.93-0.72, FeO 0-0.33-0.74.

The chemical composition of pseudomorphs differs drastically from that of the enclosing carbonaceous concretions. The concretions contain 15-20 times the quantity of insoluble residue, and higher concentrations of related components (R_2O_3, P, Fe, Mg, S, Ti, Cu, Ni, Cr, Ca, Zr, Y, Co, and Be). In the calcite of concretions there is 2-2.5 times more isomorphous Fe and Mg, more Mn, and less Sr, while the amount of C_{org} in the insoluble residue of concretions is 15-20 times smaller than in that of pseudomorphs.

By isotopic data, the carbon of pseudomorphs is associated with decomposition of organic matter, while the isotopic composition of the carbon of concretions is typical of shell material (Boggs 1972).

TABLE 2. Average Chemical Composition (%) of Pseudomorphs and Enclosing Carbonaceous Nodules

Samples	Insoluble residue	R_2O_3	FeO	CaO	MgO	MnO	SrO	P_2O_5
Pseudomorphs	2,34 / 0,93—5,32	2,11 / сл.—4,97	0,77 / 0,20—1,55	50,17 / 44,44—53,69	1,02 / 0—2,36	0,23 / 0,02—0,42	0,144 / 0,006—0,360	0,34 / 0—1,21
Nodules	36,81 / 25,97—50,56	6,36 / 4,76—7,48	1,88 / 1,15—2,42	29,09 / 20,77—25,84	1,49 / 0,77—2,65	0,18 / 0,08—0,35	0,013 / 0,021—0,118	0,56 / 0,12—1,66

Samples	SO_3	C_{org}	CO_2	Sum	$CaCO_3$	$FeCO_3$	$MgCO_3$	MnCO	$SrCO_3$	$CaSO_4$	$Ca_3(PO_4)_2$
Pseudomorphs	0,15 / 0—0,48	0,44 / 0,13—1,92	40,77 / 36,70—42,75	98,48 / 96,66—100,60	87,62 / 94,54	2,10 / 2,26	2,40 / 2,57	0,36 / 0,39	0,21 / 0,22	0,25 / —	1,10 / —
Nodules	0,21 / 0—0,48	0,44 / 0,16—0,86	23,84 / 17,94—28,40	100,90 / 97,93—99,80	49,10 / 88,39	3,12 / 5,62	3,02 / 5,43	0,29 / 0,52	0,02 / 0,04	0,36 / —	1,93 / —

Note. Numerator gives the average contents of oxides and salts, denominator the range of fluctuation of contents of the components and the ratio of carbonate salts related to the carbonaceous part of the rock. The average composition of pseudomorphs has been calculated on the basis of 22 analyses of crystals from Dutch, German, Soviet (White Sea, East Siberia, Chukotka, Kamchatka, and Sakhalin), American (Lake Lahontan and the Pacific coast), and Australian deposits. The average composition of the enclosing carbonaceous nodules has been calculated on the basis of four analyses of nodules from East Siberia and Kamchatka. Estimations of the average quantities of insoluble residue and Corg took into account the additional determinations of these components from the pseudomorphs and nodules from the United States and East Siberia. Part of the data are cited in a paper by the author deposited at VINITI (see earlier footnote).

Genesis of Pseudomorphs. The mineralogists who attempted reconstructions of the primary mineral of pseudomorphs proceeded mainly from their crystallographic characteristics. However, due to distortions of the crystallographic elements when the original mineral was replaced by calcite the measurement results were not unambiguous. This accounts for the variety of suggestions offered by various authors. Workers who had comparative material for different deposits (van Calker 1897, Dana 1885, Gurich 1901) came to the conclusion that it is difficult or impossible to identify the primary mineral with any particular mineral type known. According to E. S. Dana et al. (1885, p. 442), "the original mineral was neither gaylussite, nor gypsum, nor celestine, nor glauberite, nor one of those minerals which could have solved the problem. ... Furthermore, the original mineral seems to be unknown in nature even though it apparently was formed repeatedly in various deposits. Investigation of artificial salts of Ca, Na, and Mg grants the conclusion that none of them meets the required conditions."

Some authors made use of geological data for their reconstructions. Russel (1885), who studied the Quaternary deposit of the Lahontan Lake, unique by abundance and preservation of pseudomorphs, believed that pseudomorph (thinolite) beds 1.5-4 m thick were formed in almost the same conditions as the enclosing lacustrine limestones with freshwater lacustrine fauna. In the latter, small pseudomorph crystals were also discovered by microscopic investigation (King 1878). David et al. (1909) noted the confinement of Australian Permian—Carboniferous pseudomorphs (glendonites) to glacial—marine sediments and assumed the primary mineral to be glauberite that formed at the early diagenetic stage in liquid ooze of cold water basins. Fersman (1938, p. 625) believed that formation of the White Sea hornlets was likely to have occurred "... in the mouths of polar rivers discharging into the ocean rich in sodium chloride while the rivers carried an excess of calcium carbonate. The formation of gaylussite in the ooze of these river mouths corresponds to the low temperature of chemical processes and the high content of carbonate salts." Boggs (1972) believed that the Tertiary pseudomorphs from the western coast of the United States which he studied were pseudomorphs of calcite fillings of the crystals of rhombic carbonates formed during early diagenesis mainly in burrows. Brodskaya and Rengarten (1975), who found algal structure traces in pseudomorphs, believed them to be algal colonies that during early diagenesis were grown over by a gypsum crystal which later was replaced by carbonate.

Kemper and Schmitz (1976) hypothesized that small spherical pseudomorphs (hedgehogs) of the Valanginian and Albian of the Sverdrup basin (Canada) were formed in clay ooze of a cold Arctic basin and are a product of calcitic replacement of primary thenardite.

The foregoing data show that the primary mineral of pseudomorphs was formed in diverse tectonic (ranging from eugeosynclinal to platform), facies (from alluvial to deepsea) settings and types of sediment (from silt—clay and sand—silt to carbonaceous). In conglomerate—sand sediments, which are characterized by a high sedimentation rate, no pseudomorphs are found. The bulk of crystals are formed at the early diagenetic stage near the water-sediment contact. The typical setting for crystal development is silt—clay sublittoral sediments of a sea basin of a normal or slightly lowered salinity with abundant bentos fauna, normal aeration of bottom water, and low sedimentation rate. The major maxima of occurrence of pseudomorphs in the Permian—Carboniferous of Australia and the Quaternary of Eurasia and North America coincide with glaciations. Two other maxima — in the marine strata of Eastern Siberia and the Paleogene—Neogene of the northern Pacific Belt — occur at times of cooling when the bottom water temperature might have dropped to 0°C. Exceptions are the Triassic (?) and Permian pseudomorphs, which differ from the others by a peculiar habitus and have been formed in a warm climate at a heightened salinity, primarily at significant Mg contents (lagoonal sediment with dolomitic mineralization).

Paleogene—Neogene pseudomorph-containing sediments of the Far East also have a heightened Mg content, indicated by the presence of dolomite nodules.

All pseudomorphs except for the Upper Cretaceous Australian formations are made up of calcite. This suggests an important contribution of Ca to the composition of the primary mineral. Low Mg, Fe, Mn, and Sr contents in a great number of pseudomorphs especially in the calcite grains of an early generation indicate a low temperature during calcite formation. Specifically, a complete absence of Mg and Sr in some pseudomorphs is evidence that calcite was formed at temperatures below 12°C (Seeman 1970).

The results of study of the inner structure of pseudomorphs show them to be of a very high original porosity which amounted to tens of percent. The high porosity accounts for the friable sugarlike structure of unaltered Quaternary and some Mesozoic pseudomorphs and a considerable volume of late calcite generations which filled the cavities in the altered crystals. The high primary porosity indicates a substantial volume decrease at calcite replacement of the original mineral due to the important share of the soluble component (or the mobile phase) in its composition.

In calcite grains of the early generation, clay-organic particles are present which are distributed as concentrates over the entire grain perimeter rather than some particular side of the grain. This distribution of clay flakes is characteristic of grains (blastocrystals) created by way of recrystallization rather than free crystallization from a solution (Skropyshev 1961).

This shows that the individual formations under study are replacement pseudomorphs and not filling pseudomorphs. The probable presence of Ca in the original mineral allows us to assume that they are metamorphosis pseudomorphs.

A high organic content, sometimes up to tens of percent of the insoluble part of the pseudomorphs, and also the isotopic composition of carbon typical for organic origin are symptomatic. Evidently, this shows a significant part played by organics in creation of the primary mineral. Absence of pseudomorphs in coarse-grained conglomerate-sand rocks may be partly due to a low organic content.

The primary material of pseudomorphs thus arose in a wide range of physicochemical settings (pH, Eh, salinity). An indispensable condition usually was a low, nearly zero temperature. High Mg concentrations may have increased the temperature at which the mineral was formed and greatly modified the crystal habitus. Crystals were growing in liquid ooze near the water-sediment contact at lower sedimentation rates. The formation of the mineral was promoted by life processes of organisms, which provided heightened concentrations of reactive organic material and often made burrows in which crystals could grow readily. In the composition of the mineral, calcium and a well soluble and fast lixiviable mobile phase were important. The calcitic pseudomorph that arose after it was a metamorphosis pseudomorph.

According to V. B. Tatarskii (private communication), the primary mineral of pseudomorphs was ikaite ($CaCO_3 \cdot 6H_2O$), which precipitates at the present time from carbonate springs in cold coastal waters of Greenland (Paule 1963). This hypothesis is in a good agreement with geologic data (low formation temperatures of the primary mineral at a wide variety of other physicochemical parameters of the environment) as well as with the mineral and chemical composition of the pseudomorphs and their internal structure — the constant calcitic composition, the sometimes small or barely traceable content of isomorphous components, particularly in early generation calcite, the extremely high original porosity indicating importance of the mobile phase in the primary mineral, and signs of metamorphosis of the primary crystal into aggregate, of calcite grains. Taking into account the low stability of ikaite in surface conditions, it is legitimate to assume that its replacement by calcite occurred at the earliest stages of diagenesis. The presence of calcitic pseudomorphs in sedimentary rocks is usually a paleoclimatic indicator of low, nearly zero paleotemperatures.

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