The Mineralogical Findings in Coastal Outcrops of the Taimyr Peninsula

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Abstract. The unique mineralogical findings in the coastal outcrops of the Taimyr Peninsula have been investigated. The internal structure, mineral and chemical composition of the mineral formations have been considered. The drusoid formations were established to be glendonites, and the spherical mineral aggregates were found to compose of carbonate material mainly, the last one containing numerous inclusions of pyrite, ilmenite, plagioclase, chlorite, amphibole, apatite and barite. Due to the usage of physical and chemical modeling it is shown that the investigated mineralogical findings proved to be the result of chemical processes in the system “water–permafrost rocks”.

1. Introduction
During the trip to the Taimyr Peninsula, O. Vasik collected amazing geological samples, which aroused genuine interest among specialists and fans of mineralogical rarities. The geological formations are the druses (Figure 1 A, B, C) and nodules (Figure 1 D, E). Some of drusoid aggregates reach 1–2 cm in diameter, and their color varies from light yellowish-brown to light grayish-blue. Nodules with a diameter of 5–7 cm have a distinct zonal structure and are penetrated by micro-veins of pyrite-carbonate composition (Figure 1 E).

The described formations are localized in the rocks of the Toarchian suite of the Jurassic age which are represented by dark gray mudstones with interlayers of marls.

The zone of active water exchange in the exploration area is represented mainly by suprapermafrost waters, as well as partially subpermafrost and talik ones along river valleys. The atmospheric precipitation and the melting waters of the frozen are the source of supply of frozen water. The last-mentioned circumstance causes the high humidity of the active layer even on well-drained slopes is characterized by high humidity throughout the whole summer season. The seasonal waters are characterized by low flow rate (< 1–3 l/s) and temperature below 5° C degree Celsius. It is the composition of these waters that describes the processes occurring in the frozen rocks’ mass.

The aim of the research was to study the internal structure, mineral and chemical composition of mineralogical findings of coastal outcrops of the Taimyr Peninsula and the peculiarities of their formation.
Methods of investigation

The laboratory studies were carried out at the Analytical center of the far Eastern geological Institute FEB RAS (the certificate of accreditation no. ROSS RU.0001.518986). The determination of the element contents in the samples was carried out by means of the inductively coupled plasma mass spectrometry using Agilent 7700 c spectrometer (Agilent Technologies, USA) and the atomic emission spectrometry with the inductively-coupled plasma using iCAP 6500Duo spectrometer (Thermo Scientific Corporation, the USA). The content of H2O, loss of ignition and SiO2 was determined by means of using gravimetry. The sample preparation of solid items for the instrumental analysis was carried out in the form of open acid decomposition (HNO3+HClO4+HF).

The mineralogical studies were performed by means of the x-ray spectral microanalysis using the energy dispersive spectrometer INSA-sight produced by the Oxford Instruments company (UK) and x-ray analysis on the Dron-3 diffractometer with monochromated radiation and on the D8-Discover microdiffractometer, as well as on the Nikon Eclipse LV100 Pol light microscope.

Results of investigations and discussion

The study of the drusoid aggregates (see figure 1 A–C) in the transmitted light showed that they are composed mainly of the granoblast calcite aggregate mainly (Figure 2) with the size of some aggregates being equal to 0.1–0.2 mm. The contact of the crystals with the host coarse-grained siltstone is mostly tight with no corrosion penetration. The mineral composition of the aggregates is homogenous. The main component of the last ones is calcite (CaO = 48.65–53.76 wt. %) (table 1).

Figure 1. The forms of the formation: druses (A, B, C), nodules (D) and its cross section (E).
Table 1. Chemical composition of the mineral formations.

| Component | Unit  | Nodules (Figure 1 D, E) | Drusoid aggregates (Figure 1 A, C) | Drusoid aggregates (Figure 1 B) |
|------------|-------|-------------------------|-----------------------------------|---------------------------------|
|            |       | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| SiO₂       | wt.%  | 16.30 |0.19 | 5.78 | Zr | g/t | 68.6 | 3.10 | 23.4 |
| TiO₂       | wt.%  | 0.32 |0.01 | 0.09 | Nb | g/t | 5.01 | 0.140 | 1.35 |
| Al₂O₃      | wt.%  | 5.76 |0.08 | 1.57 | Mo | g/t | 0.799 | 0.477 | 0.321 |
| Fe₂O₃      | wt.%  | 2.35 |0.02 | 0.53 | Cd | g/t | 0.155 | 0.154 | 0.104 |
| FeO        | wt.%  | 1.76 |0.78 | 0.70 | Sn | g/t | 1.57 | 0.505 | 0.818 |
| MnO        | wt.%  | 0.38 |0.72 | 0.54 | Cs | g/t | 2.27 | 0.105 | 0.055 |
| MgO        | wt.%  | 1.62 |0.73 | 0.86 | Ba | g/t | 255.20 | 56.30 | 111.70 |
| CaO        | wt.%  | 37.85 |53.76 | 48.65 | La | g/t | 58.35 | 29.81 | 39.21 |
| Na₂O       | wt.%  | 0.75 |0.11 | 0.35 | Ce | g/t | 128.6 | 57.71 | 84.81 |
| K₂O        | wt.%  | 0.82 |<0.01 | 0.18 | Pr | g/t | 16.12 | 6.59 | 9.97 |
| P₂O₅       | wt.%  | 0.58 |0.38 | 0.48 | Nb | g/t | 69.07 | 25.37 | 38.08 |
| H₂O₂       | wt.%  | 0.93 |0.13 | 0.31 | Sm | g/t | 16.42 | 5.89 | 8.55 |
| LOI        | wt.%  | 30.11 |42.69 | 39.50 | Eu | g/t | 3.98 | 1.63 | 2.23 |
| Total      | wt.%  | 99.53 |99.61 | 99.53 | Gd | g/t | 19.25 | 7.16 | 9.63 |
| Be         | g/t   | 2.77 |0.50 | 1.23 | Tb | g/t | 3.57 | 1.23 | 1.57 |
| Sc         | g/t   | 38.40 |20.90 | 26.60 | Dy | g/t | 21.30 | 7.64 | 9.55 |
| V          | g/t   | 74.59 |8.82 | 21.08 | Ho | g/t | 4.58 | 1.70 | 2.04 |
| Cr         | g/t   | 35.03 |5.51 | 14.06 | Er | g/t | 13.05 | 5.53 | 5.91 |
| Co         | g/t   | 14.71 |1.31 | 2.6 | Tm | g/t | 1.86 | 0.798 | 0.863 |
| Ni         | g/t   | 31.71 |4.40 | 9.56 | Yb | g/t | 11.43 | 4.953 | 5.34 |
| Cu         | g/t   | 6.04 |2.44 | 4.97 | Lu | g/t | 1.74 | 0.76 | 0.826 |
| Zn         | g/t   | 47.03 |15.99 | 17.97 | Hf | g/t | 1.61 | 0.0792 | 0.471 |
| Ga         | g/t   | 7.24 |0.888 | 2.78 | Ta | g/t | 0.325 | 0.0136 | 0.126 |
| As         | g/t   | 87.65 |0.824 | 3.54 | W  | g/t | 0.823 | 0.577 | 0.412 |
| Rb         | g/t   | 28.19 |0.392 | 3.02 | Pb | g/t | 15.67 | 1.44 | 4.25 |
| Sr         | g/t   | 1132.0 |1344.0 | 1149.0 | Th | g/t | 9.45 | 8.35 | 12.26 |
| Y          | g/t   | 117.40 |45.59 | 48.93 | U  | g/t | 1.44 | 0.972 | 1.07 |

The composition and the morphology of the studied drusoid aggregates may indicate that the examined aggregates are glendonites or so – called "The White Sea flyers". The name "The White Sea
flyers" appeared due to the findings of unusual stone "hedgehogs" on the coast of the White sea, and they were classified as glendonites since they had been found in the area called Glendenbrook (the Western Australia).

The nodules (Figure 1 D) have a distinct zonal structure (Figure 1 E). Pyrite, ilmenite, plagioclase, chlorite, amphiboles, apatite, and barite are sporadically distributed in the predominantly carbonate matrix of the nodules and occur both as independent fragments and as aggregate accumulations (Figure 3 A–D, table 2).

![Image of mineral composition of calcite nodule](image)

**Figure 3.** Mineral composition of calcite nodule (kunkur): A – homoaxial pseudomorphosis of pyrite, B – dotted occurrences of pyrite, C – aggregate pseudomorphosis, D – sporadic occurrences of apatite, barite and plagioclase.

Calcite composing the nodule matrix is characterized by isomorphic inclusions of magnesium (0.59–1.37 %), phosphorus (0.25–0.59 %) and rare ones of iron. The various pyrite precipitations composing zonal homoaxial pseudomorphoses with a thin rim of the edge (Figure 3 A) are mostly widely developed in the carbonate nodule, being significantly different in composition from other forms of the manganese-containing pyrite (see the table 2). The biomorphic structure is typical for the clustered aggregates of pyrite (Figure 4). Also, there are dotted occurrences of pyrite, developing on the fragments of sedimentary formations (Figure 3 B), and aggregate pseudomorphoses on the fragments of feldspar and sedimentary rocks (Figure 3 C). The variations of pyrite compositions are not significant (table 2): they contain isomorphic inclusions of calcium (0.24–0.57 %) and quite high concentrations of manganese (0.28–1.33 %).

For a long time the formation of glendonites was associated with the process of isomorphism and calcite substitution of various mineral formations, among which geylussite, glauberite, gypsum, celestine, anhydrite, tenardite were more often mentioned as the primary mineral [1]. Recently according to the information from the scientific literature, ikait has been considered to be the precursors of glendonites [2–6, etc.]. Glendonites are viewed as pseudomorphoses formed from icaite and,
therefore, are the product of substitution of icaite’s crystals (CaCO₃·6H₂O) by dense aggregates of calcite without changing its shape (CaCO₃). There is also an alternative explanation indicating that the glendonite occurred among carbonate-free rocks as the result of microbiochemical activity and ingestion of organic carbon or methane of biogenic origin into the precipitation from underlying deposits [7–14, etc.].

Table 2. Chemical composition (wt. %) in the mineral inclusions according to the data of x-ray spectral microanalysis.

| Mineral        | Spectrum | O   | Na  | Mg  | Al  | Si  | P   | S   | K   | Ca  | Mn  | Fe  |
|----------------|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Pyrite         | 1        | –   | –   | –   | –   | –   | –   | 51.29| –   | 0.24| –   | 44.29|
| Pyrite         | 3        | –   | –   | –   | –   | –   | –   | 52.16| –   | 0.57| 0.28| 45.00|
| Pyrite         | 5        | –   | –   | –   | –   | –   | –   | 52.30| –   | –   | 1.33| 44.81|
| Ilmenite       | 2        | 36.09| –   | 0.17| 0.19| –   | –   | 1.15 | 0.59| 33.80|
| Calcite        | 4        | 42.28| 1.31| –   | –   | 0.59| –   | 37.61| –   | –   | –   | –   |
| Calcite        | 10       | 46.49| 0.81| –   | –   | 0.58| –   | 38.25| –   | 0.29| –   | –   |
| Calcite        | 11       | 46.26| 0.59| –   | –   | 0.25| –   | 39.37| –   | –   | –   | –   |
| Calcite        | 12       | 46.43| 1.37| –   | –   | 0.54| –   | 37.94| –   | 0.70| –   | –   |
| Plagioclase    | 6        | 50.28| 7.67| –   | 11.55| 30.20| –   | 0.16| 2.07| –   | –   | –   |
| Plagioclase    | 7        | 50.56| 8.60| –   | 10.39| 31.06| –   | 0.91| –   | –   | –   | –   |
| Plagioclase    | 14       | 50.04| 3.60| –   | 10.32| 30.27| –   | 8.32| 0.81| –   | –   | –   |
| Plagioclase    | 17       | 53.44| 4.27| –   | 8.43| 25.85| –   | 5.65| 7.38| –   | 0.27| –   |
| Chlorite       | 8        | 63.22| 1.07| 20.92| 25.05| –   | 0.24| 1.48| –   | 1.95| –   | –   |
| Chlorite (?)   | 16       | 44.52| 3.95| 4.13| 9.32| 0.31| –   | 3.51| 19.02| 6.45| –   | –   |
| Amphibole (?)  | 9        | 48.48| 0.36| 4.10| 8.31| 12.08| –   | 0.75| 4.92| 0.23| 20.85| –   |
| Barite         | 13       | 29.62| –   | –   | –   | 3.80| 0.31| 13.44| 1.56| –   | 1.50| –   |
| Apatite        | 15       | 41.35| 0.48| 2.05| 3.80| 11.82| 0.19| 0.84| 30.92| 0.73| –   | –   |

Note: 1) – not found; 2) in addition to the above said, additional elements in the following minerals are detected: apatite (spectrum 15) – F = 5.69 %; ilmenite (spectrum 2) – Ti = 31.49 %, V = 0.37 %; chlorite (?) (spectrum 16) – Cr = 0.86 %; barite (spectrum 13) – Sr = 4.96 %, Ba = 49.99 %; 3) analyst G. B. Molchanova.

But, in any case, it is obvious that the studied aggregates were formed as the result of the interaction of water with rock. They are precipitated from the solution with a possible involvement of biologically mediated process.

Precipitation of carbonate minerals is a thermodynamically controlled process complicated by the kinetics of reaction in a medium with non-ideal interaction, variable substrates, pH fluctuating, organic molecules and gas, phase interactions. Taking the above mentioned complication into consideration, however, the fundamental reason of forming the solid calcite is the (necessity of) presence of sufficient concentrations of Ca(aq)³⁺ and CO₂(aq)²⁻ in the supersaturated solution.

Understanding the genesis of the mineralogical findings of the Taimyr Peninsula is a matter of understanding what processes contribute to the supersaturation of the precipitation and the solution of carbonates. The physical-chemical simulation of the water-rock (W/R) system based on the minimization of the Isobaric–isothermal potential (Selector-Window software package [15]) was performed to create conditions leading to the formation of a supersaturated solution. The method of the simulation consisted in performing the series of calculations of the equilibrium state of the water-rock system. The bulk composition of the water-bearing rocks calculated according to the number of moles of each component was used as a source material. As the result of simulating the conditions of the formation of groundwater composition of permafrost low–mineralized calcite-un saturated HCO₃–Ca waters were established to be formed at the W/R ≤ 0.004 / PCO₂ = 10⁻².⁰ mass ratio. However, with increasing salinity and alkalinity of waters (TDS > 0.6 g/dm³, pH > 7.4) the last ones become saturated.
with calcium carbonate, which is removed from the solution in these conditions. Equilibrium with some other compounds forming secondary mineral phases (plagioclase, chlorite, amphibole, apatite, barite, and pyrite and ilmenite) is also achieved. These conclusions are in good agreement with the provisions of S. Shvardsev [16] and others concerning the behavior of basic cations in groundwater of different landscape zones.

Calcium is one of the first to be deposited from groundwater in the areas of interest. And thus sodium attains a capacity of being accumulated in water. Such elements as Fe, Al, Si$^{2-}$ are low-mobile in slightly alkaline solutions, so the accumulation of the first ones is not observed, but these components give rise to new mineral phases (table 2). The forming neocrystallisations remove both major components and a lot of other elements, such as V, Sc, Cr, Ni, As, Zn, Sr, Ba, Ce, Pb and others (see table 1) from the solution.

It is obvious that a special role here belongs to the intensity of water exchange, which determines the total amount of salts in the solution and depends mainly on the quantity of the rock involved in the dissolution, i.e. the area of interaction of the rock with water and is regulated by the processes of periodic freezing and thawing of the active layer too.

4. Conclusion
Thus, mineralogical findings of coastal outcrops of Taimyr Peninsula have been investigated. The internal structure, mineral and chemical compositions of mineral formations have been considered. The drusoid formations were established to be glendonites, and the spherical mineral aggregates were found to compose of carbonate material mainly, the last one containing numerous inclusions of pyrite, ilmenite, plagioclase, chlorite, amphibole, apatite and barite. For calcite, composing the noodle’s (kunkur’s) matrix, isomorphic inclusions of magnesium, phosphorus, rarely iron are characteristic. Due to the usage of physical and chemical modeling the investigated mineralogical findings proved to be the result of chemical processes in the system "water–permafrost rocks", which depend mainly on the amount of the rock involved in the dissolution, i.e. the area of interaction of the rock with water and are regulated by the processes of periodic freezing and thawing of the active layer too.

Further investigation of mineralogical findings of the Taimyr Peninsula can be useful for stratigraphic constructions and paleogeographic reconstructions of this area of interest. It's not unlikely that the signs of the methane sips from relic gas hydrate deposits or other natural gas accumulations will be detected in the underlying strata of permafrost.

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Figure 4. Biomorphic structure of pyrite.
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