Manifestation of infiltration–metasomatic processes in the Kazanian stage sediments of the Lobach Mountain in Tatarstan

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Abstract. For the first time in the Kazanian stage evaporate sediments of the Kama-Ustyinsky structure, metasomatites were identified confined to bituminous accumulations zones. Metasomatites develops in microgranular sedimentary-diagenetic dolomites. The main dense core of metasotatic bodies is composed of marble-like calcite, along periphery of which there is ferriferous goethite-hydrogoethite edge. Numerous calcite veins extend from carbonate core to sides, their thickness decreases with distance from metasotatic bodies. In the zone of metasomatites development, processes of gypsum lenses recrystallization and siliceous nodules dissolution, originally found in microgran dolomites, are observed. The small size siliceous nodules are completely leached and replaced by calcite aggregates. Larger flints partially pass into translucent chalcedony and aggregates, consisting of large quartz crystals - clear rock crystal. The formation of metasomatites is due to aggressive hydrocarbon-containing fluids introduction into the rocks, as indicated by their spatial confinement to bituminous accumulations.

1. Introduction

The Kama-Ustyinsky structure is brahiantiklinal uplift, complicating the southern part of the Kazaklar arch. In the modern relief, it is expressed by a dome with absolute elevations of 160-180 m [1]. Being in confluence of the Volga and Kama rivers, the uplift forms a ledge of the Volga Upland, better known as the mountain of Lobach. The slopes of ledge facing to river and partially cut off by water stream. As a result, over 4-5 km along the coast in cliffs reaching a height of up to 20 m, outcrops of gray-colored marine sediments of the Upper Kazanian stage are observed.

Starting from the Volga River water's edge in the Lobach mountain outcrops, a successive change of layers is observed. Pechishchinskian, Upper Uslonian and Morkvashian strata of the Upper Kazakhstanian stage, in accordance with accepted regional stratigraphic scale, are divided into smaller geological unit - bands. Directly near the water edge dense, light gray dolomites with gypsum lenses are exposed in cliff walls, which in the local stratotype correspond to band B (“layered stone”). Above them lies a 1.5 - 2.0 m thick layer of greenish-gray, weakly cemented sandstones of the C band (“cutting”).
In the outcrop wall sand layer is bends in waverly, then rises to a height of 2.0 m above the water edge, then completely immersed in water. Upper to the section, sandstone is replaced by light-gray, weakly gypsified dolomites of band D (“gray stone”). Within the band, there is layers alternation composed of dense dolomites, broken by systems of cracks into large blocks, with layers of highly fragmented comminuted vertically fractured dolomites, less often brecciated dolomites. Among dolomites, inclusions of siliceous nodules in the form of various sizes lenses are observed, which form intermittent horizons stable along to the littoral. Next comes band E (“shihan”) is represented by a relatively thick (≥5.0 m) layer of light gray hard gypsum dolomite, which, unlike the band D rocks, is characterized by more dense and massive structure. In the E band roof, in some zones, metasomatic transformation of the initial rocks, this is manifested in replacement of dense gypsum dolomites to brecciated limestones with ferritization. Above the E band dolomites bed terrigenous-carbonate deposits of the F band (“gaize”) with a thickness of 2.0 m, which are change to oolitic limestones and gypsified dolomites of the G band (“podluzhnik”) with a total thickness 5.0 m. Completes the Upper-Kazanian section in the outcrops of the Lobach mountain, band H (“transitional”). It is relatively easily detected by the presence in its sole of a 0.5 meter greenish-gray layer folded by dolomite marl, in which thin (up to 2.0 cm) layers of green clay are noted. Up the section marl layer is replaced by light gray dolomites. This is, in general terms, the Upper-Kazanian section of the Lobach mountain. The red-colored continental deposits of the Urzhumian stage, represented by marl-clay strata, are everywhere bedded on the Upper-Kazanian stage rocks.

Throughout the geological history, from its formation moment of to the present, sedimentary deposits of the Upper-Kazanian stage were in fact in near-surface conditions, without experiencing deep dives. Thus why, all post-depositional changes previously observed in the rocks were associated either with diagenesis stage or with superimposed hypergenesis processes during the period when rocks entered to aeration zone. With diagenesis associated partial crystalline modification of aphanitic dolomite with formation of hypidiomorphic crystals up to 0.05 mm in size, siliceous nodules and celestine nests new growth too [2]. Corrosion of dolomite crystals, formation of small (up to 0.1 mm) xenomorphic calcite grains filling the voids and cracks in dolomite, as well as rare precipitation of iron hydroxides is include to postdiagenesis processes [3]. Most of these transformations are spatially associated with surface water percolation zones.

2. Results

Taking into account the spatial confinement of the object to tectonic calm platform zone, it is difficult to assume the presence of any epigenetic manifestations associated with endogenous processes in the Upper Kazanian stage deposits. However, studies conducted in recent years have established bituminous manifestations and extensive development of metasomatic processes in the Lobach outcrops, which can in no way be caused by exogenous factors.

Metasomatic processes are most pronounced in the D band lower part on contact of dolomite layer with the C band sandstone. Here, almost over every elevated section of sandstone wave-like bed, in dolomites metasomatosis phenomena are recorded. Metasomatites are vein-shaped bodies with a straight, horizontal sole and convex top. In cross section, they look like a single-convex lens with flat base (figure 1). The average width of the cores in the lower part is from 3.0 to 4.5 m, and the thickness in the most convex part is from 1.5 to 2.5 m. Within the veins, microgranular dolomite is completely replaced by hard, marble calcite. In some cases, the veins are composed only of calcite, in others, along with calcite, iron hydroxides are also present, mainly represented by goethite (α-FeOOH). Depending on the presence or absence of goethite, veins color can vary from light gray to brown. Within veins themselves, goethite is unevenly distributed, its sequential decrease from the bottom to up is observed. As a result of this, veins in the lower part are painted in a dark brown color, and in the upper part - in light gray. According to optical microscopic studies, veins composed of marble-like calcite are characterized by a medium-
coarse-grained structure and a uniform texture. The rock consists entirely of xenomorphic calcite crystals that are in close contact with each other, inside of which are separated grains, or larger relict aggregates of substituted dolomite. At the calcite grains boundaries interspersed ferrum oxide are noted.

In outcrops, metasomatites sharply differ from enclosing them dolomites, not only in mineral composition, but also in their physicomechanical properties. If dolomites are a highly fractured rock, easily crumbling under hammer blows, then metasomatic veins, on the contrary, are dense, hard formations from which hammer bounces with a sound. The host rocks various properties and metasomatites also determine various resistances to exogenetic processes. As a result of this, in the Lobach outcrops, lenticular entities appear, against the general background of retreating slopes in the form of small isolated hills.

![Photo metasomatite vein in the D band dolomites](image)

**Figure 1.** Photo metasomatite vein in the D band dolomites

Around the marble-like calcite veins, the initial dolomite rock also underwent a metasomatic transformation at varying degrees. On average, metasomatites influence zone on host rocks is about 6.0 m. Within this zone, dolomites are penetrated by multiple veins that cut them along the stratification and consisting of regular spherical shape calcite grains. In addition, all calcite spheres have almost the same size ~ 1.0 mm. Near the main bodies, calcite veins thicknesses averages 5.0–6.0 cm with a length of up to 1.0 m. Along perimeter around a marble-like calcite veins in a radius of 2.0 m, one can often observe how individual veins are intertwined or connected by vertical jumpers, forming an openwork mesh texture (figure 2). However, as the veins move away from the main body core, their thickness and length gradually decrease. And at a distance of 5.0-6.0 m, they are detected only in the form of thin and intermittent shoelaces located at a great distance from each other.
Figure 2. Photos of calcite veins along the metasomatic body’s periphery.

The host dolomites and siliceous nodules contained in them, which fell into the zone of metasomatites influence, also underwent a metasomatic transformation. The intensity and nature of siliceous nodules change was largely determined by their size and remoteness from the marble-like calcite veins. The small size (<3.0 cm) siliceous nodules close to the veins, were completely leached, and new cavities formed in their place were filled by epigenetic calcite. Larger flints underwent only partial leaching. Either one or several sides of the nodules were subjected to leaching process. It’s depending on how passed filtration channels of the solutions to nodules location. Holes and etching channels which elongated parallel to the aggressive solutions filtration paths are always detected on leached surfaces (figure 3).

Figure 3. Photos of siliceous nodules that have fallen into the metasomatites influence zone.

Siliceous nodules located at some (4.0–6.0 m) distance from the veins of marble-like calcite, along with dissolution processes, were also subject to very intense recrystallization. On the leached surfaces of siliceous nodules, as well as in cavities of leached large caverns, fairly large (5.0-10.0 cm in diameter) nests of clear quartz were formed. Many cavities have a zonal structure, which manifests itself in a sequential increase in quartz crystals size as they move away from siliceous nodules walls. In the same direction, the number of quartz crystals habit elements is increasing. In some cases, quartz crystals of outer zone reach to size 3.0–5.0 mm. All quartz crystals are oriented perpendicular to growing surface.
A completely different character of source rocks metasomatic transformation is observed in the marble-like calcite veins bottom part. In particular, poorly cemented, loose sandstone of the C band, near metasomatites becomes extremely hard and resistant to mechanical stress. Such physicomechanical properties changes are due to the intense sandstone calcitization in the metasomatism local zone. The entire void-pore space of sandstones is filled with large (> 5.0 mm) calcite grains, which function as poikilitic cement of basal type. Calcite zones are, as a rule, enriched with ferrum oxide, which give sandstones a brown color, which stands out against a general greenish-gray background. The calcitization zone usually has small thicknesses from 0.5 to 1.0 m. Along the calcitization zone outer perimeter, a thin (0.1–0.3 m) zone of ferritization is detected, represented by red lenses and layers of goethite.

It should be noted, that within the metasomatite formation area, under marble-like calcite veins and between them, the entire layer of greenish-gray sandstone contains reddish goethite layers that give a banded texture to the rocks. In some cases, goethite layers form a peculiar eye texture due to the presence of reddish goethite layers in greenish-gray rock.

Metasomatic transformations also touched the lowest in outcrop dolomite layer of the B band. Everywhere, dense, light gray dolomites with white gypsum lenses directly beneath the marble-like calcite veins have undergone severe ferritization. The most intense ferritization is associated with gypsum lenses, which are so saturated by α-FeOOH that they have acquired a dark brown color. These gypsums, unlike unchanged ones, underwent a very significant recrystallization, which resulted in replacement of granular gypsum (alabaster) by aggregate which consisting of large (from 2.0 to 8.0 cm) translucent gypsum crystals - iceland spar.

The metasomatic nature of marble-like calcites bodies’ formation is confirmed by the following structural features.

1. Sharp transitions of dolomites to marble-like limestones along the strike of rocks.
2. Local development of marble-like limestones within the dolomite layer.
3. The presence of relics of grains and aggregates of the initial dolomite in calcite grains composing marble-like limestones.
4. Siliceous nodules leaching with complete or partial replacement into calcite aggregates.
5. Substitution of initial dolomites into marble-like limestone with volume preservation.

3. Discussion

Given the presence in upperlying the E band dolomites of bituminous layers, the metasomatites formation can be represented as follows. At the boundary of the Late Paleozoic and Early Mesozoic [4], long-lived regional faults intersection zones on the Volga-Ural anteclise territory often served as channels for vertical migration of fluid hydrocarbon-containing solutions [5]. As a result, contrasting hydrochemical anomalies were formed in overlying rocks, leading to epigenesis transformations of host rocks, which were accompanied by a complete or partial change in their structural-material composition [6].

Lobach is one of the peaks of the Kama-Ustyinsky structure which is tectonically associated with intersection zone of sublatitudinal the Kama fault with a series of parallel lineament zones of
submeridional strike [7]. Being practically at the deep faults intersection it could not but experience the ascending gas-liquid flows influence.

Judging by the nature of the conversion of biomicrite dolomites, the water expelling stage solutions interacting with them were characterized by increased biological activity, since under normal thermodynamic conditions, CaMg(CO$_3$)$_2$ is much more stable than CaCO$_3$ to external influences. This regularity is violated only in bacterial activity processes, where there is a redistribution of the substance with the participation of microbial communities [8]. Sahibgareev R.S. [9] noted that in oil systems dolomite stability is much lower than calcite.

The formation of relatively large (0.5-1.0 mm) calcite crystals in metasomatic veins and their uniform granularity over entire volume of veins indicates that metasomatism proceeded process of at a very slow rate. Relicts of Initial dolomites which captured by calcite indicate about synchronicity processes of rock dissolution and newly formed structure crystallization and injectable character of replacement front propagation. In addition, the absence of structural defects in calcite grains like as growth zones or twinning indicates preservation of stationary conditions of the crystallization environment during metasomatites formation. Apparently, the main role in redistribution of carbonate substance was assigned to Ca$^{2+}$, Mg$^{2+}$, Fe$^{2+}$ and HCO$_3^-$ ions diffusion migration in pore space solution which filling intergranular space of dolomite rock. In this case, Mg$^{2+}$ was removed from system and Ca$^{2+}$ and Fe$^{2+}$ ions were additionally introduced, making up for volume deficit. In absence of ions external influx, the metasomatites would be composed of loose calcite mass. The hydrocarbonate ion, obviously, controlled the crystal-forming environment acid-base balance, determining direction of “dissolution-synthesis” process. In a simplified form, the metasomatism process can be described by following stages: biochemical dissolution of dolomite → increased alkalinity of solution due to increase in Ca$^{2+}$ and Mg$^{2+}$ ions concentration; leaching of siliceous nodules → calcite grains formation and growth both chemogenous oxidation of Fe$^{2+}$ and goethite formation.

A distinctive feature of the identified metasomatites from other similar formations is absence of metasomatic column clearly defined mineralogical zonality. Only the alkaline zone of metasomatism, represented by marble-like calcite, is sufficiently pronounced. The late acid stage is weakly manifested as rare goethite precipitates form on contacts marble-like calcite with sandstone and gypsum lenses ferritization in host dolomites. This metasomatites structure is explained by carbonate specific of system and, mainly, carbon dioxide composition of influrance solutions, which determine mobility of limited alkaline earth metal ions amount.

4. Conclusion

To summarize the above, we can formulate following conclusions:

1. Infiltration-metasomatic processes, expressed in replacement of initial rocks with marble-like calcite, are widely developed in the Upper Kazanian stage sediments of the Kama-Ustyinsky structure;

2. The metasomatic bodies of marble-like calcite form veins with flat, horizontal sole and convex roof, unconformable lying among sedimentary rocks of the Upper Kazakh stage;

3. Two geochemical zones in metasomatites can be traced: alkaline, forming the limestone core of vein bodies and acid, forming peripheral margin in form goethite aggregates;

4. Formation of metasomatism is due to influence of hydrocarbon-containing fluids into rocks, as indicated by their spatial confinement to bituminous accumulations.
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