Vein-rock in the «Dark kingdom» Marble Deposit (South Ural) and their Possible Connection with Gold Ore Mineralization

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Abstract. During the geological training of RUDN students in the Miass district of the Chelyabinsk region, one of the abandoned open stone quarry for the extraction of crushed marble was studied. Examination of the walls of the stone quarry revealed a wide development of vein and dike bodies spatially associated with the apical part of the Syrostan granitoid massif. The noted vein and dyke complexes are accompanied by halos of skarn, greisen, and pegmatite mineralization, which allows us to consider the Dark Kingdom deposit as a promising object for identifying valuable minerals, including gold.

1. Introduction
The Dark Kingdom field is located 15 km northwest of the city of Miass, a large industrial center in the Southern Urals. In geological terms, it is formed by lenticular marble bodies of the Urenginsky Formation of Riphean age, which are in the form of xenoliths in the apical part of the Syrostan granitoid intrusion. The Syrostan intrusion is spatially confined to the zone of the Main Ural deep fault and is a multiphase structure formed during the Lower Carboniferous. The first phase is granodiorites and quartz diorites, the second is double-feldspar, substantially plagioclase granites. The third phase is a vein complex. [1-6]. According to [7-12] the vein complex of the intrusion includes the mineralization of tantalum-niobates, fluorite, beryl, gold. So, the aim of this research was to clarify the prospects for localization at the Dark Kingdom deposit, in addition to marble, and other noted ore minerals.

2. Materials and methods
The factual material for the research was the mapping data and the results of testing the rocky outcrops of the rocks of one of the stone quarry that revealed a large marble lens. Samples were studied using microscopy (polarized microscope POLAM L213M), X-ray phase (diffractometer DRON-4) and emission spectral (spectrograph DFS-8) analyzes. Analyzes were carried out in the laboratories of RUDN University, Russian State University of geological prospecting (RSUGP) and the Experimental and methodological expedition in Alexandrov.
3. Results and discussion
Mapping has shown that metamorphogenic, magmatogenic and dike-vein rock complexes are involved in the structure of the deposit.

The metamorphogenic complex, in addition to the main marble body, consists of its scattered numerous small fragments, which are enclosed in the form of xenoliths among diorite rock. The border between diorites and marbles is of a mixed type: in some places it is winding with distinct signs of injection absorption of marbles by penetrating diorite magma. In other cases, the border is straight and smooth, coinciding with slip joints, which indicates its tectonic nature. Marble is light gray to white, of varied grain sizes with calcite grains from 0.5 mm to 1 cm. In some cases, the rock is banded due to graphite flakes (Figure 1). In thin sections, it is composed of isometric calcite grains with frequent polysynthetic twins of tectonic slip (Figure 2). Marble is mainly without impurities, but in the near-contact zones, may include disparate secretions of tremolite, epidote, and quartz. The average chemical composition of marble (%): SiO$_2$ -2.01; Fe$_2$O$_3$-0.03; Al$_2$O$_3$- <0.01; MgO -0.35; Na$_2$O -0.02; K$_2$O- <0.01; CO$_2$- 42.26 [13]. The amount of impurity noticeably increases when xenoliths of marble are accompanied shists (Figure 3). They are quartz-biotite, carbon, and biotite-quartz; the microtexture is thin-flaky, lepidoid and granoblastic.

The magmatogen complex is exposed on the north and northwest sides of the stone quarry, where the relationships of these formations with metamorphogenic and vein-dyke rock are clearly shown. The complex includes quartz diorites, granodiorites, and biotite granites. Quartz diorites and granodiorites are macroscopically difficult to distinguish. They are characterized by a fine-grained texture, massive structure, as well as a characteristic greenish-gray color, which is formed by numerous dotted inclusions of colored mineral. Often in such rock relic inclusions of incompletely remelted xenoliths are present (Figure 4). In thin sections, quartz diorites and granodiorites are represented by biotite differences. The main minerals in them, in addition to biotite (15-20%), are quartz (15-25%), potassium feldspar (~ 5%) and plagioclase. In diorites, plagioclase is mainly zonal, with external zones corresponding to oligoclase-andesine (Figure 5). In granodiorites, plagioclase corresponds to twin oligoclases. Of accessory minerals, sphene, zircon, apatite, epidote, and zoisite are established. The content of chemical elements in the rock: K$_2$O- 4.21; CaO – 5.67; Fe$_2$O$_3$-7.86. Biotite granites are gray medium-grained porphyry rocks of a massive, spotted, and banded structure. They are composed of potassium feldspar - 45% (cannelated and pertite microcline) (Figure 6), andesine-oligoclase (15%), quartz (30%), biotite (10%). The texture is hypidiomorphic-grained with a predominant idiomorphism of feldspar grains.

Figure 1. Banded texture in marble xenoliths.
Figure 2. Twins gliding in calcite, thin section, polars crossed. Field of view 0.25 mm.
Figure 3. Shists at the base of marble xenolith.

Figure 4. Schists xenoliths in diorite rock.
Figure 5. Segregation of zonal plagioclase in quartz diorite. Field of view 1.0 mm, polars crossed.
Figure 6. Segregation of cancelled microcline in biotite granite. Field of view 2.0 mm, polars crossed.
Accessory minerals include sphene, zircon, apatite, epidote. Transitions from biotite granites to diorites are poorly noticeable (gradual) (Figure 7). The content of chemical elements: K₂O – 2,83; CaO-3,01; Fe₂O₃-3,42.

The dike-vein complex is spatially closely related to the diorites and the marble xenoliths enclosed in them. It is represented by granitoid and lamprophyric formations, as well as quartz veins.

The granitoid vein phase includes porphyritic granite, microgranite, microgranodiorite and aplite (?) varieties [14]. The chemical composition of the rock is unstable and varies within: K₂O- 4,09 - 8,21; CaO - 6,06-28,0; Fe₂O₃ - 1,27-1,05. The vein morphology depends on the host rock. In diorites, these are injections of a complex shape and different sizes (Figure 8). In marble xenoliths and along their contacts with diorites, these are ribbon-shaped straight or bending bodies that coincide with joints of separate sub-latitudeinal and submeridional strike. Also, there are secondary formations of skarnified and greisenized rock. The thickness of the veins is from the first centimeters to 0,5 m. Their composition is of the same type and is determined by the variable ratios of quartz, acid plagioclase and potassium spar. The quantitative variations of the minerals are variable, which is why the granitoid composition of the minerals changes several times down dip and undip. Accessory minerals - sphene, zircon, and epidote are constantly found in thin sections.

In some cases, the vein bodies of granitoids acquire a pegmatoid appearance due to the development of large (2-5 cm) inclusions of pink potassium feldspar in their central part.

**Figure 7.** Gradual transition from quartz diorites to biotite granites, most likely, through the granodiorite zone.

**Figure 8.** Injection of veined granitoids into diorite rocks.

**Figure 9.** Large crystal of orthite in microgranites of a vein complex. Field of view 0,25 mm., plain polarized light.

Sulphide mineralization in the form of thin streaks of pyrite and chalcopyrite is also noted here in vein selvage. Scarnoids are represented by calcareous and silicate varieties. Usually they are developed in the near-contact zones of marbles with vein granitoids, where they form narrow rims from millimeters to first centimeters. In some cases, in tectonically disturbed marbles, skarns are set in the form of nests and pockets with a diameter of up to 2.5 m. The color and structure of the skarnified rock are spotty and banded with a predominance of green and pink color shades. The structure is uneven grained with mineral grains from fractions up to 7 mm. The main dark-colored minerals are epidote with chlorite, as well as small-scaled green hornblende. In the form of relics, replaced feldspar, chloritized pyroxene, and possibly vesuvianum are preserved to varying degrees. Bunnies of pink garnet appear in skarnified granitoids with crystal sizes up to 7 mm Thus, the list of noted mineral phases reflects the unstable (intermittent and multidirectional) nature of the skarn process. This, obviously, explains the joint presence in the rock of minerals of such different temperature and metasomatic facies. Of note are cases of late superimposed albization of skarns, vein granitoids, as well as previously described quartz diorites. This process is accompanied by the appearance of streaks and inclusions of pyrite, chalcopyrite and molybdenite (?) .

Greisenization is recorded only in vein granitoid bodies of relatively high thickness with thicknesses of about 0,5-1,0 m. A quartz-muscovite aggregate develops here with mica flakes up to 1 cm in size. In thin sections, muscovite, pseudomorphically replaces biotite, and, together with secondary mosaic quartz, destroys feldspars and quartz grains of the original granitoids. The process is accompanied by the appearance of non- twinned albite, which forms various accretions with other
minerals. In most cases, greisenisation is intermittent. It increases in some vein bodies and weakens in others, but it never reaches its full realization. Usually it degenerates into lower-temperature processes of sericitization and berizitization. In these variants, fine and fine-scaled muscovite (sericite) is actively developing along feldspars, so that from many grains only their external contour is preserved. Along the way, biotite is replaced by chlorite, clinozoisite and epidote. A characteristic mineral of such rock is its cerium variety - orthite. In thin sections, the orthite is brown, with a high relief, often well-faceted and has a zonal structure (Figure 9). In rock where berizitization is developed, along with sericite, a fine-grained aggregate of secondary quartz, small carbonate inclusions, and dispersed pyrite inclusions appear.

Lamprophyric formations for the Syrostan granitoid massif are described for the first time. They are represented by dikes of kersantites and odinities [14] with a thickness of 0.2-0.5 m. These are late formations associated with faults, by which slips of diorites and granitoid vein bodies occurred (Figure 10). Macroscopically, odinities are black, cryptocrystalline dense rock of massive structure with dispersed thin inclusions of sulfides. In thin sections, odinities are composed of green amphibole (60-65%), plagioclase (20-25%), chlorite, and thin-flaked biotite. Plagioclase is mostly replaced by an epidote-zoisite aggregate and albite (Figure 11). The content of chemical elements in the rock: K₂O - 1,74; CaO – 9,97; Fe₂O₃ – 9,79.

![Figure 10. The black dyke of spessartites filling the disjunctive dislocation in marbles and diorites.](image1)

![Figure 11. The microstructure of spessartites. Field of view 0,5 mm., plain polarized light.](image2)

![Figure 12. Cave-like voids in a quartz vein filled with ferruginous ochers.](image3)

Unlike the odinities, kersantites are fine-grained mica rock, which easily decompose into thin chips when weathering. In thin sections, instead of amphibole (10%), coarse-flaky biotite (20-25%) becomes the main colored mineral. Both minerals interchange each other, which indicates their simultaneous crystallization. Plagioclase is of several generations. The latest of them, albite, together with quartz, corrodes the matrix of the rock. Of accessory minerals, sphen, zircon, apatite, epidote are established. A quartz bedding rein is mapped in the western side of the stone quarry. In other places vein quartz is found in the form of large amounts of debris and rock fragments. The thickness of the vein is 1,5-2 m. The vein runs along the steeply rising contact of biotite schists and vein granitoids. A characteristic feature of the quartz vein is the wide development of pores and deep caverns filled with ferruginous matter. Many pores have distinct cubic contours preserved from leached sulfide minerals. In some cases, small fractions of partially oxidized pyrite are observed in individual fragments of quartz. Leaching processes are especially powerful in the floor of vein at its contact with the shists. Large cave-like voids up to 1 m deep filled with ferruginous ochre are found there (Figure 12). According to the data of spectral analysis, such ochers contain abnormally high Mo concentrations (0.03%) and elevated Ag contents (6 *10⁻⁵)

To identify the geochemical features of the rock, sampling of the quarry walls was done. Depending on the degree of exposure, the distance between the sampling points varied from 2 to 10 m. One to six samples were taken at each point, considering the hypsometric position of the petrographic types of rocks mapped in the quarry wall. A total of 92 samples were taken, which were studied by atomic emission quantitative spectral analysis. 37 elements - impurities were determined. Of these, because of low concentrations, Ba, As, Sb, W, Ta, Yb, Hf, Cd, In, Tl, and Hg turned out to be of little information. Data on the remaining elements are shown in table 1. As can be seen from the table,
except for marbles, a characteristic feature of the rock formations of the Dark Kingdom deposit is the obvious similarity of their geochemical appearance. This is reflected both in a close set and in comparable concentrations of trace elements contained in them. The most striking geochemical features of magmatic formations include intensive accumulation of phosphorus in the rock, the amount of which is an order of magnitude or higher than the clarke of the element in igneous rocks. Significant contamination of the rock Co, Cr, V, Cu, Zn, Pb and especially Mo is also indicative of magmatites. In the latter case, considering the above clarke concentrations of the element, we can obviously speak of the molybdenum specialization of the magmatic melt. Another important feature of the geochemistry of magmatic complexes is the constant, albeit insignificant (below clarke) presence of Ti, Mn, B, Sn, Li, Nb. In addition, attention is drawn to the abnormally low (lower than the sensitivity of the analysis) concentrations of barium, rare earth elements and yttrium, which are typical

Table 1. Trace elements content in rock of the Dark Kingdom deposita.

| elements          | Rock complexes and element content (ppm) | marbles | diorites | biotite grani | veined granite | shists | Lamprophyres | veined quartz and ochres | skarns |
|-------------------|-----------------------------------------|---------|----------|---------------|---------------|--------|--------------|--------------------------|--------|
| Cu                | 2.5/0.6                                 | 23/0.7  | 25.4/1.3 | 18.5/0.9      | 29.0/5.0      | 32.5/0.9| 39           | 65                       |        |
| Zn                | -                                       | 78.3/1.1| 67.5/1.1 | 40/0.7        | 93.5/1.2      | 80/1.1  | 44           | 70                       |        |
| Pb                | 2.6/0.3                                 | 22.5/1.5| 18.9/0.9 | 26.1/1.3      | 20/1.0        | 7/0.5   | 9.2          | 90                       |        |
| Mo                | -                                       | 1.1/1.2 | 1.32/1.3 | 1.38/1.4      | 1.01/0.5      | 0.3/0.3 | 30           | -                        |        |
| Ag                | -                                       | -       | -        | -             | 0.11/1.1      | -       | 6            | -                        |        |
| Ni                | 2.9/0.1                                 | 14.9/0.3| 10/1.3   | 8.4/1.1       | 26.2/0.3      | 60/1.1  | 24           | 8.5                      |        |
| Co                | -                                       | 9.4/0.9 | 7.9/1.6  | 4.5/0.9       | 15.1/0.8      | 22.5/2.2| 8.2          | 6.5                      |        |
| Cr                | -                                       | 41.8/0.8| 31/1.2   | 30.8/1.2      | 28.5/2.8      | 160/3.2 | 82           | 30                       |        |
| V                 | -                                       | 77/0.7  | 84/2.1   | 40.8/1.0      | 147/11.3      | 175/1.7 | 121          | 65                       |        |
| Ge                | -                                       | -       | -        | 0.6/0.4       | 1.1/0.6       | -       | 5.5          | -                        |        |
| Ga                | -                                       | 20/1.0  | 21.5/1.1 | 15.8/0.8      | 18.2/0.6      | 11/0.6  | -            | 12.5                     |        |
| Ti                | 1.3/0.0                                 | 27.1/0.03| 39.9/0.2 | 18.1/0.1      | 43.5/0.01     | 45/0.1  | 1.5          | 17.5                     |        |
| Mn                | 240/0.2                                 | 334/0.5 | 285/0.5  | 338/0.6       | 562/8.4       | 900/0.7 | 465          | 1000                     |        |
| P                 | -                                       | 2210/13.8| 2400/34.3| 761.5/11      | 2125/270      | 300/18.8| 350          | 300                     |        |
| Sr                | 409/0.7                                 | 61/0.8  | -        | 30.8/0.1      | 232/5.2       | 150/19  | -            | 250                     |        |
| B                 | -                                       | 6.4/0.4 | 5.6/0.4  | 8/0.5         | 5/0.3         | 3.5/0.2 | 5            | 18                       |        |
| Sn                | -                                       | 2.6/0.9 | 2.6/0.9  | 2.6/0.9       | 2.6/0.9       | 2/0.7   | 1.5/0.5      | 3.5                      |        |
| Zr                | 47/2.5                                  | 81.8/3.2| 88.5/4.0 | 66.1/0.3      | 934/4.7       | 80/3.1  | 64           | 115                     |        |
| Li                | -                                       | 8.1/0.4 | 3/0.8    | -             | 18.1/0.3      | 0.5/0.3 | -            | -                        |        |
| Nb                | -                                       | 9/0.5   | 10.2/0.1 | 12.6/0.6      | 9.7/0.4       | -       | -            | -                        |        |
| Y                 | 14/0.5                                  | -       | -        | -             | -             | -       | -            | -                        |        |

Number 23  20  12  18  9  2  5  4

*a* Notes: in the numerator is the average content of the element; in the denominator is a clerk of his concentration. Italics highlight the values of elements whose concentrations are higher than clarke. Clerk concentrations were calculated relative to clarks according to A. P. Vinogradov [15]; for marbles - relative to clarks according to K. Turekian and K. Wedepohl [16]; (-) - contents below the sensitivity of the analysis. The sensitivity of the spectral analysis: Cu 1*10^{-3}, Zn 1*10^{-3}, Pb 1*10^{-3}, Mo 1*10^{-3}, Ag 1*10^{-3}, Ni 1*10^{-3}, Co 1*10^{-3}, Cr 1*10^{-3}, V 1*10^{-3}, Ga 1*10^{-3}, Ge 1*10^{-3}, Ti 1*10^{-3}, Mn 1*10^{-3}, P 1*10^{-3}, Sr 1*10^{-3}, B 1*10^{-3}, Sn 1*10^{-3}, Bi 1*10^{-3}, Zr 1*10^{-3}, Li 1*10^{-3}, Nb 1*10^{-3}, Y 1*10^{-3}.

trace elements for such rocks. A specific feature of the chemical composition of diorites, granites, and vein granitoid complexes is also a sharply low strontium content. Its concentration is two to three times lower compared to similar rocks in the central part of the Syrostan massif [8]. Given the close spatial relationships of magmatic formations and xenoliths of marbles and slates enclosed in them, their trace elements are compared. As follows from Table 1, a fundamentally similar picture of the distribution of trace elements is observed in magmatites and shists and is sharply different in relation to marbles. Compared to others, these rocks are characterized by a limited set of trace elements (Cu, Pb, Ti, Mn, Sr, Zr, Y, Ni) and their very low contents. The exception is zirconium, whose
concentrations are more than two times higher than clarke contents. The presence of Mn, Sr in marbles is not surprising. These elements are common to any calcite rock, since for it they are the main isomorphic impurities. As for other impurities and, especially, Zr, their presence, albeit in small quantities, apparently reflects a low degree of metasomatic effect of introduced magmatic melts on marble.

Judging by the Zr concentrations (Table 1), the activity of metasomatism in the initial stages was relatively high and was acidic in nature, which facilitated the migration of the element in the form of complex sulfate and fluoride-ion compounds [17,18]. Most likely, this process coincided in time with the granification of granite rocks, which was also associated with the activity of acid solutions. On the other hand, abnormally low concentrations of Sr in magmatites serve as an indicator of a weak metasomatic effect of marbles on them, even in those areas where rocks are in contact with each other. Thus, the aforesaid leads to the conclusion about the low prospects of metalliferous calcareous skarnoids. Unlike marbles, the geochemical parameters of shists do not fundamentally differ in their parameters from igneous rocks. As can be seen from Table 1, Zn, Pb, Cr, V, Mn, P, Sr, and Zr accumulate above clarke here. At the same time, these elements are just as characteristic of magmatogenic complexes, concentrating in them both below and above the clarke level. Moreover, in most cases, in absolute values, their concentrations are not inferior to shists. The noted signs suggest an active metasomatic process that existed between shists and magmatites. Therefore, there is reason to consider silicate skarnoids as concentrators of valuable metals. Important indicators of shists also include Li, P, Sr and Ag. The contents of these elements significantly exceed their amounts in relation to any igneous rocks. Of note are the concentrations of phosphorus (more than 2%) and silver (1,1*10^5 %). In both cases, for the rock of the Syrostan massif, these elements in such quantities are noted for the first time. Mentioning the prospects of silicate skarnoids for mineralization, one should once again pay attention to their chemical composition (Table 1). Judging by the triad of chalcophilic elements (Cu, Pb, Zn), these rocks can include significant ore mineralization. The validity of this conclusion is confirmed by the results of the stone quarry mapping. During these studies, vein and disseminated excretions of chalcopyrite-pyrite aggregates were identified. Finally, the presence of Mo and Ag in quartz veins is of paramount importance (Table 1). The appearance of silver (6*10^5 %) is usually considered as an important prospecting indicator for gold mineralization. As can be seen from table 1, top-cut grade concentrations (at the industrial level) of Mo (3*10^2 %) are no less significant for such samples. Given these facts, additional studies have been conducted.

Using the methods of X-ray phase and X-ray fluorescence analyzes, iron-ferrous ocher products of weathered quartz veins were studied. Unexpected results were shown by X-ray phase analysis. On the diffraction patterns. Only reflections of aluminosilicate phases are recorded, but there are no signs of Fe oxide minerals. However, the typical rusty color of the samples confirms their presence, as well as chemical analysis do. According to it, the content of Fe,O₃ in the samples is from 20 to 25%. The above facts prove the development of iron oxides in the form of X-ray amorphous colloidal compounds. Such iron oxides indicate an adsorption mechanism of Mo accumulation. Finally, important data were obtained by X-ray fluorescence using a Clever C-31 spectrometer. In several samples, the gold content was recorded at the level from the one to ten ppm (Figure 13). From this perspective, the studies of the material composition of the rocks, as well as the geological features of the studied territory, do not confirm the previously expressed opinion [19] about the futility of the Syrostan granitoid massif for gold bearing.
Figure 13. X-ray fluorescence analysis patterns with rather high gold content.

4. Conclusion
The results of studying the area of the abandoned stone quarry give reason to consider the Dark Kingdom marble deposit as a promising object for prospecting for the possibility of detecting industrial gold mineralization.

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