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Research Article

MINERALOGICAL SIGNS OF ORE-BEARING CAPACITY OF EARLY CARBONIFEROUS VOLCANOGENIC FORMATIONS OF PALEOVOLCANOES OF SOUTHERN UZBEKISTAN

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ABSTRACT
In this article, the ore potential of early carboniferous volcanic rocks of paleovolcanoes of Southern Uzbekistan for non-ferrous (Cu, Pb, Zn) and noble (Au, Ag and platinum group metals) metals is presented on the basis of the results of microprobe studies of the forms of occurrence, the material composition of accessory ore minerals, ore-bearing silica-alkaline fluid microsegregations and nanocrystallites in them. The connection with rocks of around-vent and vent facies of rhyolite paleovolcanoes of Southern Uzbekistan is shown for pyrite-polymetallic mineralization (Cu-Pb-Zn-Au-Ag-Pt*).

Keywords: *Andesites, Dacites, Rhyolites, Concentrator Minerals, Carrier Minerals, Ore-Generating Fluid Microsegregations, Pyrite-Polymetallic Mineralization*

INTRODUCTION
In Southern Uzbekistan, especially on the southwestern spurs of the Gissar Range, the study of the patterns of evolution of volcanism and associated mineralization remains an important problem. At the same time, issues related to the development of mineralogical criteria for the metallogenic specialization of rocks of vent and around vent of lower carboniferous paleovolcanoes are of particular relevance. The last ones are very important for the relatively poorly studied Khojabarku-Malyangur (Vakhshivar), Kyzylmechet, Karasan and other paleovolcanoes due to the fact that today they are highly promising for mineral resources (Mamarozikov *et al.*, 2022).

MATERIALS AND METHODS
To identify the mineralogical features of the early Carboniferous volcanogenic formations of paleovolcanoes of Southern Uzbekistan, responsible for the formation of pyrite-polymetallic mineralization with a noble metal load (Cu-Pb-Zn-Ag-Au-Pt*), the following studies were carried out: petrographic and mineralogical study of thin sections of rocks and ore formations using a Nikon Optiphot 2Pol multifunctional polarizing microscope; study of the form of occurrence and composition of rock-forming, accessory, ore minerals and ore-generating fluid inclusions preserved in them on an electronic microanalyzer JXA - 8800R "Superprobe" (Japan).

RESULTS AND DISCUSSION
The volcanogenic formations of these paleovolcanoes were formed under conditions close to those of volcanic islands, as evidenced by the presence of marine terrigenous and carbonate rocks in them. The variety of forms of manifestation of volcanic activity was expressed in the unequal facies composition of volcanics, represented by tuffs, tuff breccias, agglomerates (explosive facies), lavas and lava breccias (effusive facies), eruptive dikes and injection tuffisites (extrusive facies). Along with rocks formed as a result of the ejection or outpouring of deep-seated material onto the surface, volcanic rocks that do not reach to the surface (subvolcanic facies) are widespread. Numerous sill-like deposits and large laccolith-like bodies of andesite-dacitic and rhyolitic porphyries are noted at all paleovolcanic structures in the region (Shayakubov *et al.*, 1988).
To date, in Southern Uzbekistan, number of ore objects (about 50 ore occurrences and deposits) have been identified in Early Carboniferous volcanic-sedimentary formations (Ore deposits, 2001).
According to P.V. Pankratyev (1971), the main type of deposits corresponds to pyrite-polymetallic or Altai. From geochemical data on the distribution of lead and zinc it is clear that in unaltered rocks of the rhyolite formation these elements are everywhere below clarke value, but in the zones of altered rocks of the vent,

around vent and subvolcanic facies, their quantity increases sharply, which gives grounds to consider the rocks of the named facies favorable for the accumulation of copper, lead and zinc. It has been established that the position of ore deposits in the section of sedimentary-volcanogenic strata is determined not only by structural, tectonic and magmatic factors, but also by the composition of the constituent rocks. Pyrite-polymetallic mineralization is clearly associated with volcanic bodies of the rhyolite formation of the lower carbon (Pankratev, Mikhailova, 1981).

The main accessory ore minerals of various types of rocks of volcanic facies are: pyrite, sphalerite, galena, chalcopyrite, magnetite, titanomagnetite, ilmenite, rutile; non-metallic ones - quartz, plagioclase, potassium spar, sericite, chlorite, carbonates. In ore-bearing metasomatites after volcanics, in addition to endogenous minerals, supergene mineral formation has also become widespread, where copper minerals also dominate: azurite, malachite, chrysocolla, covellite, cuprite, chalcanthite, etc. Leading and trace elements in them were previously mainly given based on the results of bulk chemical analyzes of sulfides (Pankratev, Mikhailova, 1981). We offer new results of microprobe studies of the main carrier minerals and mineral concentrators of ore, especially non-ferrous, noble and rare earth elements in volcanics and associated hydrothermal-metasomatic formations.

Pyrite – is the most common sulfide mineral in volcanics and associated metasomatites and ores of paleovolcanoes in Southern Uzbekistan (Fig. 1). It is associated with many sulfides, which replace it along the cracks of crushed crystals. In pyrites, according to P.V. Pankratiev, Yu.V. Mikhailova (Pankratiev, Mikhailova, 1981), impurities were identified: silver (0-124 g/t), gold (0-9.84), tellurium (up to 4. 4 g/t), indium (up to 1.42), gallium (up to 2.3 g/t), germanium (less than 0.5 g/t), arsenic (up to 400 g/t), cadmium (in single samples 198 g/t), bismuth (320, in single samples up to 900 g/t), cobalt (up to 110 g/t), nickel (up to 900 g/t). As a result of our microprobe studies in pyrites of acidic volcanics of the studied paleovolcanoes of the region, it was established (in%): Cu - 0.02-0.12; Ni – 0.05-0.25; Co – 0.00-0.03; Zn – 0.00-0.15; Zn – 0.00-1.25; As – 0.04-1.04.

Chalcopyrite – is a common sulfide mineral; its content in ore-bearing metasomatites of the Early Carboniferous volcanics of the region ranges from 0.05 to 6.1%. It is found in association with sphalerite, galena and pyrite. According to microprobing data, impurities of zinc (1.5%) and lead (0.36%) were found in chalcopyrite.

Sphalerite – is one of the main sulfide minerals of all types of volcanics and associated metasomatites, its content in ores reaches up to 50%, it predominates over galena. Their ratio in ores varies from 1.5 to 5.2. Of the impurity elements in sphalerites, the most interesting are cadmium (1831-3980 ppm), indium (up to 81.9 ppm), gallium (up to 118 ppm), germanium (up to 25), for which it is a mineral - carrier. Other impurities include selenium, gallium, bismuth, as well as silver and gold (Pankratev, Mikhailova, 1981). According to microprobing data, it was established in sphalerites (in%): Cu - 0.13-1.67; Ni – 0.00-0.08; Co – 0.02; Mo – 0.00-3.38; platinoids – 0.00-0.50; Cd – (0.34-0.74) and iron (0.22-2.53).

Galena – is one of the most important sulfide minerals in terms of abundance. According to microprobing data, it was established in galena (in%): Ag - 0.29-0.34; Ni – 0.08-0.12; Co – 0.08-0.12; Zn – 0.15-1.25; platinoids – 0.28-0.73; Fe – 0.12-0.34.

Complex supergene oxides of copper, zinc and tin are found in processed volcanic-sedimentary rocks by solfataric-fumarolic action, in particular secondary quartzites after acidic volcanics. They are often associated with malachite in the vicinity of copper-zinc-bearing quartz-hematite veinlets.

Timmanite – mercury selenide (in%, Hg - 59.34-69.92; Se - 27.42-31.92) was determined in silicified rhyolites of the Kyzylmechet paleovolcano (Fig. 2).

Apatite, monazite, siliceous hydromonazite, xenotime are the main phosphate minerals that are concentrators of rare earths and carriers of radioactive elements.These minerals are also carriers of silver, zirconium and hafnium. For example, an admixture of hafnium (HfO_2 - 0.11%) was found in the chlorapatites of the rhyodacite eruptive dyke of the Khojabarku-Malyangur paleovolcano, and in the xenotime of secondary quartzites on rhyodacites - zirconium (ZrO_2 - 9.25%) and hafnium (HfO_2 - 0.23%). Siliceous basaltic andesite monazite contains hafnium (HfO_2 – 1.92%). In monazite of quartz-hematite-chlorite metasomatites, an admixture of silver (Ag_2O - 0.36%) was detected after andesite; Felsite porphyry monazite is a carrier of zirconium (ZrO_2 – 0.99%) and hafnium (Hf_2O – 0.15%). Monazite crystals of explosive rhyolite breccia are silver-containing (Ag_2O – 0.61%). Zirconium impurities (ZrO_2 – 0.63%) were determined in the xenotime

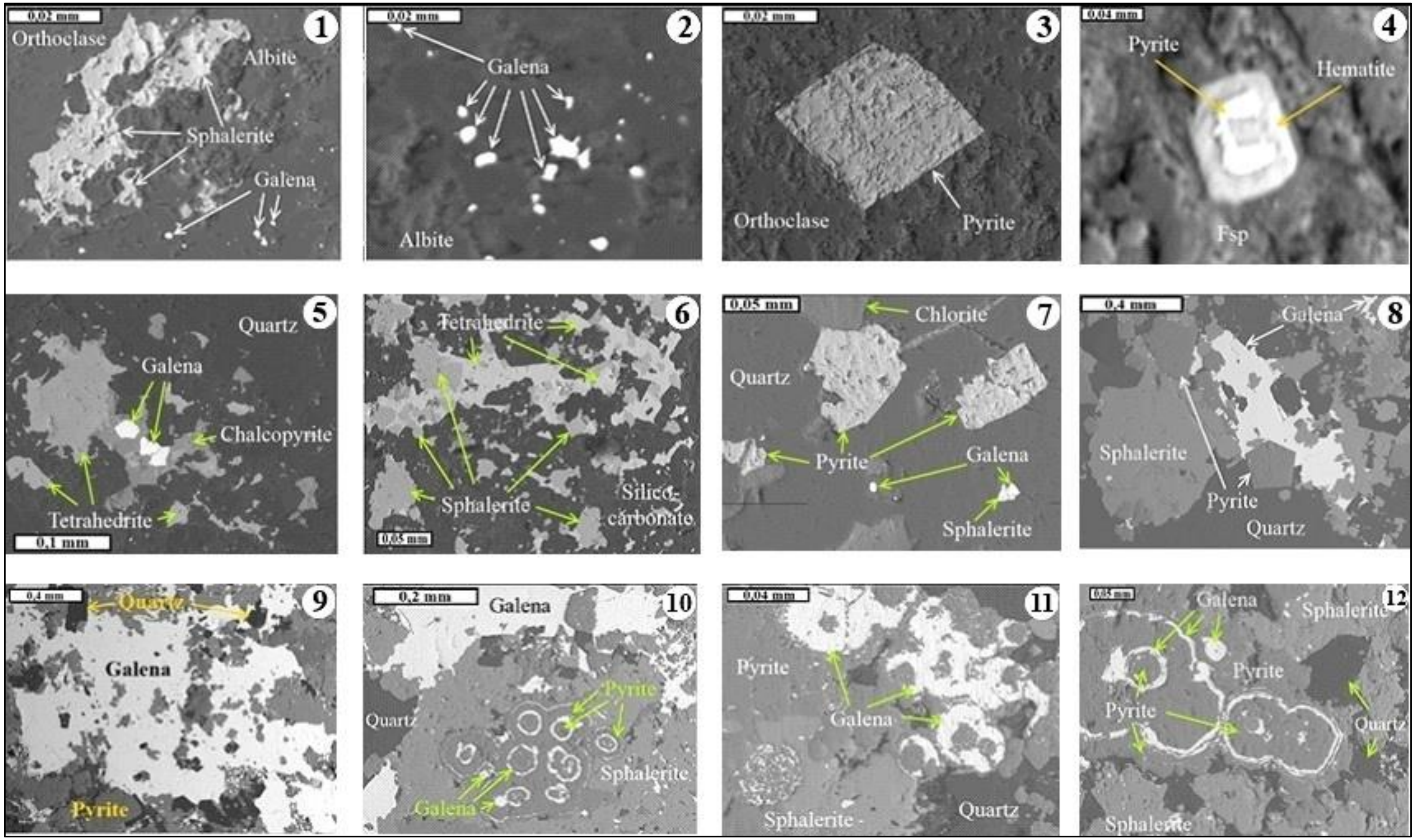

Figure 1. – Forms of occurrence of sulphide minerals in volcanogenic-sedimentary rocks of the Khodjabarku-Malyangur (VKh), Karasan (KN) and Kyzylmechet (KM) paleovolcanoes (Southern Uzbekistan): 1-5 – sulfides of eruptive dikes of rhyodacite (1-4) and rhyolite (5) (VKh): 1 - sphalerite-galena paragenesis; 2 – inclusions of galena microcrystals in albite; 3 – inclusion of pyrite in orthoclase; 4- replacement of pyrite with hematite; 5-6 – sulfides in rhyolite clastolava (KN): 5 – galena-chalcopyrite-tetrahedrite association; 6 – forms of occurrence of sphalerite and tetrahedrite in the siliceous carbonate mass; 7 – pyrite-galena-sphalerite association in vitroclast tuffaceous rhyolite (KM); 8-12 – textural and structural features of Pb-Zn pyrite ores associated with acid volcanics (KN).

of crystalloclastic rhyolite tuff. Single grains of boron-containing hydromonazite (B_2O_3 - 19.55%) were found in tuffaceous siltstones of acidic composition. In secondary quartzites developed along acidic volcanics of the near-vent facies of the Karasan paleovolcano, plumbogummite - lead aluminophosphate (in%, SiO_2 - 7.11-17.25; TiO_2 - 0.00-0.89; Al_2O_3 - 22.65-23.11; P_2O_5 - 14.07-14.56; SO_3 - 0.00-8.15; CuO - 0.00-0.41; ZnO - 1.30-1.52; PbO - 33.86-35.33) and pyromorphite - lead chlorophosphate (in%, Al_2O_3 - 4.34; P_2O_5 - 15.72; Cl - 2.65; PbO - 67.52), associated with malachite.

Carbonate minerals of the early Carboniferous volcanics of the region are represented by calcite, manganesecarbonate, ankerite, siderite, cerussite (lead carbonate) and smithsonite (zinc carbonate) in the form of segregations, amygdalae and veinlets. Calcite, ankerite and siderite in andesites, rhyodacites and rhyolites of the Khojabarku-Malyangur paleovolcano are carriers of rare earth metals (TR_2O_3 0.26-10.13%). In rare cases, calkinsite and lanthanite (Fig. 2) appear in these rocks, which belong to their own carbonate minerals-concentrators of rare earths (TR_2O_3) and thorium carriers (ThO_2 - 1.72-5.80%). In addition, impurities of tellurium (TeO - 4.30-5.25%) and silver (Ag_2O - 5.21%) were detected in the phosphorus-bearing calkinsites of the Khojabarku-Malyangur paleovolcano. The siderites of secondary quartzites developed along the near-vent acidic volcanics of the Karasan paleovolcano contain the following impurities (in%): CuO - 5.33-12.19; PbO – 0.00-1.40; ZnO – 2.53-3.98.

Silver minerals in acidic volcanics are represented by sulfosilicates, silver sulfocarbonates, basaltic andesites and andesites - copper and zinc-containing oxidized silver minerals, which were studied by microprobe studies. In sulfosilicates and sulphacarbonates, the silver content varies from 34.90 to 80.41%, and in the latter - from 7.24 to 57.70%. Oxidized silver minerals containing admixtures of tellurium, sulfur and chlorine are found in the tuffaceous siltstones of the Karasan paleovolcano. In the andesites of this palevolcano, microprobe studies have revealed a microinclusion of native silver containing impurities of tellurium (0.30%), gold (0.15%), palladium (0.82%), sulfur (1.88%) and chlorine (3.09 %).

Zirconium and hafnium minerals – zircon, calciozircon, cyrtolite and hydrocyrtolite - are found in all petrographic types of volcanic rocks of the early carboniferous paleovolcanoes of the region (Fig. 3). They belong to mineral carriers of rare earth (0.00-8.43%) and radioactive elements (UO_2 - 0.00-2.58%; ThO_2 - 0.00-5.74%). In a single case, a zircon crystal containing osmium (OsO_4 - 12.94%) was identified in the basaltic andesites of the Khojabarku-Malyangur paleovolcano.

Yttriolite, a yttrium silicate and a carrier of rare earths, was identified for the first time in the rhyolite clastolavas of the Khojabarku-Malyangur paleovolcano. **Chevkinite** found in rhyodacites, thorianite in basaltic andesites of the Khojabarku-Malyangur paleovolcano also belong to the mineral carriers of rare earth elements (in %, 11.12 and 4.20, respectively).

Orthite - found in almost all types of volcanics, studied paleovolcanoes and belongs to silicate minerals-concentrators of rare earths (TR_2O_3 - 27-57%), carriers of yttrium (Y_2O_3 - 0.00-3.49%) and thorium (ThO_2 0.00 -4.26%). Silver (Ag_2O – 0.12-0.15%) was determined in orthites of clastolava and eruptive breccia of rhyolites.

Oxide minerals of iron and titanium in early Carboniferous volcanic-sedimentary rocks of the region and metasomatites developed after them are represented by magnetite, titanomagnetite, ilmenite, rutile, hematite and goethite. They can be classified as carrier minerals of Zr, Hf, Sc, Cu, Zn, Ag and platinoids. For example, in the rutile of rhyodacite of the Khojabarku-Malyangur paleovolcano there are impurities of zirconium (ZrO2 - 0.16%) and hafnium (HfO_2 - 0.60%), and the rutile of siliceous limestones that have magmatic contact with rhyodacites contains impurities of magnesium, zirconium and hafnium (in%, ZrO_2 - 3.72; HfO_2 -0.50); in rutiles of quartz-hematite-chlorite metasomatite from andesites and secondary quartzites from rhyolites of the same paleovolcano, an admixture of scandium was detected (Sc_2O_3 - 0.16% and 0.46%, respectively). Impurities of copper (CuO – 5.07%), zinc (ZnO – 3.76%), sulfur (SO3 – 0.16%), and phosphorus (P_2O_5 – 2.26%) were determined in the goethite of the acid tuff siltstone of the Karasan paleovolcano. Impurities of platinum (Pt -1.08%) and zinc (ZnO - 0.60%) were detected in single rutile grains of acidic tuff siltstones of Khojabarku-Malyangur. Hematite, in secondary quartzites after rhyolite, is a carrier of copper, zinc, arsenic and sulfur (in%): CuO – 2.28; ZnO – 1.94; As_2O_5 – 0.44; SO_3 – 5.04.

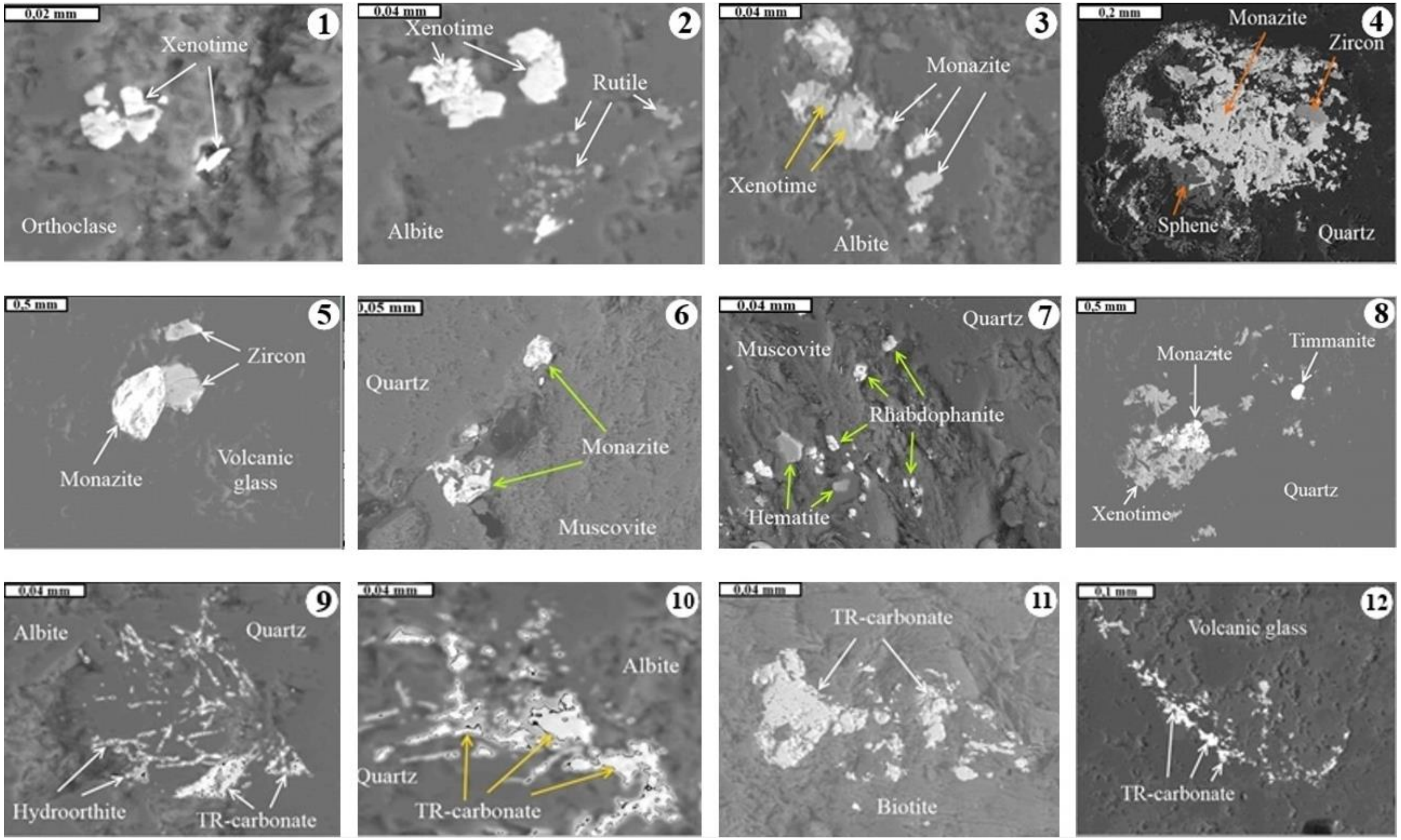

Figure 2. – Forms of occurrence of xenotime, monazite and rhabdophanite – phosphate minerals-concentrators of rare earth elements, timmanite – mercury selenide and lanthanite, calkinsite – hydrocarbonates of rare earth elements in volcanic rocks of the Khodjabarku-Malyangur (VKh) and Kyzylmechet (KM) paleovolcanoes (Southern Uzbekistan): 1- inclusions of xenotime in a phenocryst of orthoclase of silicified rhyolite (VKh); 2 – xenotime and rutile in rhyodacite albite (VKh); 3 – relationship of xenotime and monazite in andesidacite albite (VKh); 4 – form-occurrence and relationship of monazite with zircon and sphene in rhyolite clastolava (VKh); 5 – zircon-monazite paragenesis in volcanic glass of rhyolite (KM); 6 – monazite in silicified quartzite after rhyolite (KM); 7 – rhabdophanite in eruptive breccia of rhyolite (KM); 8 – paragenesis of timmanite with monazite and xenotime in silicified rhyolite (KM); 9-11 – lanthanites in rhyolite clastolava (VKh); 12 – calkinsite in silicified quartzite after rhyolite (VKh)

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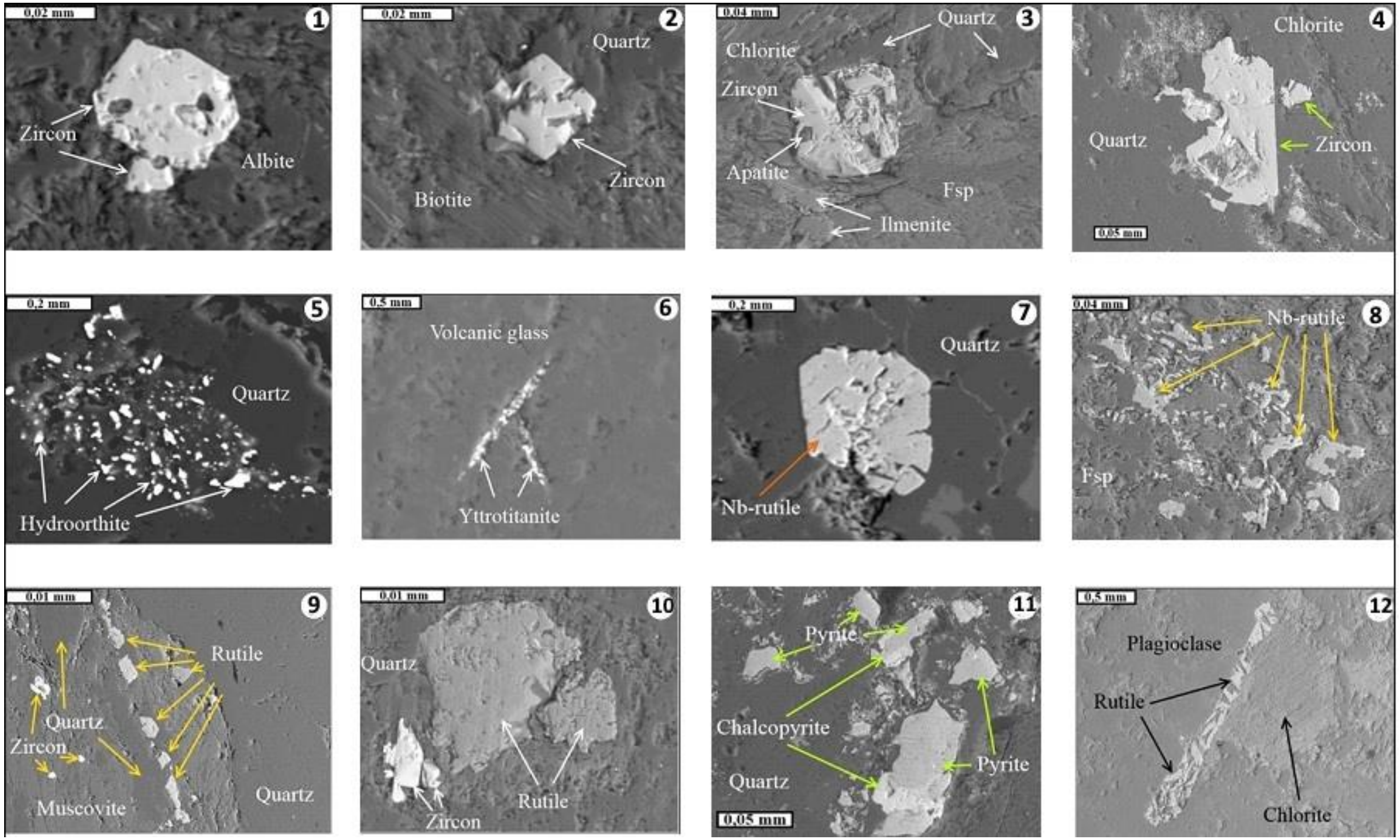

Figure 3. – Forms of occurrence of zircon, hydoortite, ytrotitanite, rutile in volcanic rocks of the Khodjabarku-Malyangur (VKh), Karasan (KN) and Kyzylmechet (KM) paleovolcanoes (Southern Uzbekistan): 1-2 – zircon crystals in an eruptive rhyodacite dike (VKh); 3 – mineral paragenesis of zircon with apatite and ilmenite in felsic porphyry (VKh); 4 – corroded zircon grain in eruptive rhyolite breccia (KM); 5 – "ore dust" of hydroorthite in muscovite clastolava (VKh); 6 – clusters of ytrotitanite microcrystals in cracks in volcanic glass of hyaloclastic rhyolite lava (KM); 7-8 – Nb-rutile in clastolava (7) and eruptive rhyolite dike (8) (VKh); 9 – relationships between rutile and zircon crystals with quartz and muscovite in tuffaceous siltstone (KN); 10 – paragenesis of rutile and zircon in the quartz-muscovite matrix of silicified rhyolite (KN); 11 – paragenesis of rutile with pyrite and chalcopyrite in a quartz phenocryst of clastolava rhyolite (KN); 12 – relationship of acicular rutile with plagioclase phenocryst in rhyolite (KM).

Barite in the volcanic-sedimentary rocks of the studied paleovolcanoes can be attributed to the mineral carriers of lead (0.00-0.37%), zinc (0.00-1.18%), in rare cases gold (Au - 0.44%) and rare earths (TR_2O_3 – 7.74%).
Anglesite and alamosite are supergene minerals of the oxidized zones of deep hypogene lead ores. We studied the mineral paragenesis of anglesite with malachite and hematite in secondary quartzites developed after rhyolites of the Karasan paleovolcano. Alamosite was identified in hydrothermal-metasomatically reworked volcanics of the Khojabarku-Malyangur, Kyzylmechet and Karasan paleovolcanoes. In many cases they are carriers of silver, gold, tellurium, copper, arsenic, radon and platinum group metals. For example, impurities of tellurium (TeO-1.21%), silver (Ag_2O - 0.40%), ruthenium (Ru_2O_3 - 0.86%) and radon (Rn - 1.48%) were detected in the alamosite of the clastic lava of the Khojabarku-Malyangur rhyolite, Alamosites of quartz-chlorite-hematite metesomatite after andesite contain platinoids (%, Ru_2O_3 - 1.28; Rh_2O_3 - 1.39; Pd - 0.06), silver (Ag_2O - 0.30%), gold (Au -0, 30%) and arsenic (As_2O_3 – 0.38%).
For the first time, ore-generating **silica-alkaline chloride fluid microsegregations containing sugar-like nanocrystals**, which are carriers of copper, lead, zinc, silver, osmium and platinum group metals, have been established in clastolavas, exposure breccias of rhyodacites, rhyolites and secondary quartzites developed along them. This is confirmed by significant concentrations of silver, platinoids and radon in chlorine-containing silica-alkaline fluid microsegregations preserved in rhyolite clastolavas and eruptive rhyodacite dikes of the Khojabarku-Malyangur paleovolcano (%, respectively, Ag_2O - 0.11 and 0.31; PGE - 0.26 and 1.20; Rn –1.26). The sugar-like alamosite nanocrystallites they contain are characterized by high concentrations of silver, osmium and platinoids (%, Ag_2O - 0.35; OsO_4 - 1.43; platinoids - 3.75). Nanocrystals of high-chloride (Cl - 22.09-28.40%) silicon-alkaline (SiO_2 - 9.52-18.13%; Na_2O - 0.00-23.98%; K_2O - 9.12-42.13%) microsegregations , determined in crystallastic tuffs of rhyolite composition of the Karasan paleovolcano, also differ in their specialization for zinc (ZnO - 2.19-4.53%), silver (Ag_2O - 0.17-0.38%) and elements of the platinum group (PGE - 0.15-1.85%). Silica-alkaline microsalts identified in explosive breccias of rhyolitic composition contain nanocrystals of silver sulfosilicate.

CONCLUSION
Thus, mineralogical signs of ore-bearing properties of early carboniferous volcanic rocks of paleovolcanoes of Southern Uzbekistan for non-ferrous (Cu, Pb, Zn) and noble (Au, Ag and platinoids) metals have been identified based on the results of microprobe studies of the forms of occurrence, material compositions of the main mineral concentrates, carrier minerals ore elements, ore-bearing silica-alkaline fluid microsegregations and nanocrystallites in them. A paragenetic connection with rocks of around-vent and vent facies of rhyolitic paleovolcanoes of Southern Uzbekistan is shown for pyrite-polymetallic mineralization (Cu-Pb-Zn-Au-Ag-Pt*).

REFERENCES
Mamarozikov UD, Normatov UA, Khamraev A Kh, Saitov NE, Suyundikova GM (2022). On the problem of identifying the metallogenic specialization of paleovolcanoes of Southern Uzbekistan. *Geology and Mineral Resources*. **4**. 16-21.
Shayakubov T Sh, Dalimov TN, Arapov VA, Shpotova LV, Korzhaev VP (1988). Volcanism of the Western Tien Shan. *Tashkent: Fan.* 328.
Rep. editor Golovanov IM (2001). Ore deposits of Uzbekistan. *Tashkent: GIDROINGEO*. 611.
Pankratiev PV, Mikhailova Yu V (1981). Ore formations of stratiform lead-zinc deposits of Uzbekistan. *Tashkent: Fan*. 252.