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***Research Article***

# MANGANESE -ORE MINERALIZATION OF THE UPPER-EOCENE-LOWER OLIGOCENE (MIDDLE TIEN SHAN, CHATKAL-KURAMA ZONE, UZBEKISTAN)

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## ABSTRACT
Upper Eocene-Lower Oligocene stratiform manganese ore occurrences of initially-sedimentary metagenesis are studied. Oxidic minerals of manganese (oxydic, carbonaceous) on litological-facial formation and to paragenetical indexes were formed in neritic-sea (arctic) conditions. In the ores are present interesting quantities of noble (Au, Ag, Pd), non-ferrous (Cu, Pb, Zn, etc.), rare, rare-earth ($REE_{Ce+Y}$+Y), U and others (Cr, Ni, V, etc.) strategic metals.

***Keywords:*** *Pyrolusite, Cryptomelane, Manganite, Gold, Platinum Metals, Rare Earths*

## INTRODUCTION
Geological and industrial types of deposits and ore occurrences of manganese in Uzbekistan (Golovanov, 2001; Strakhov *et al*., 1968; Chekunov, 1962, 1963) are represented by Upper Eocene-Lower Oligocene primary sedimentary (stratiform) ore occurrences, volcanogenic-sedimentary (Llandovery-Wenlock, Silurian), telethermal and epigenetic (Mesozoic-Cenozoic), hydrogenic-hypergenic-residual (remnants by modern weathering crusts), metamorphogenic (lower Paleozoic) types of mineralization (Table 1).

**Table 1: Geological Industry Typing Deposits and Occurrences of Manganese Uzbekistan**

| Geological and Genetic Typing (Morphology of Ore Bodies) | Facial-Formational Affiliation | | Deposits, Ore |
|---|---|---|---|
| | Formations | Manganese | |
| Volcanic-sedimentary (lenses, seams, seams, sheet-like body) | Carbonate: Primary oxide, siliceous limestone | Psilomelane-pyrolusite, psilomelane-vernadite, braunite- hausmannite | Ziyatdin, Dautash, Kyzylbayrak, Tersaksay, Chupanata. |
| Intraplate (platform-sedimentary) stratiform-singenitic-diagenitic: | Terrigenous: Primary oxide, peroxide. | Cryptomelane-pyrolusite, psilomelane-new pyrolusite, manganite. | Qazanbulaq, Gavasay, Karaalma. |
| disseminated (oolites, interlayers, lenses, seams, sheet-like body). | Carbonate: carbonate-oxide. | Psilomelane-pyrolusite new manganocalcite (psilomelane)-pirolyuzite. | Mazar. |
| Telethermal-epigenetic (veins, peel, smears). | Volcanic carbonate: oxide, carbonate-oxide. | Psilomelane-new with pyrolusite and rhodokhrosite mangano calcium loads. | Sidzhak, Taskuduk, Chupanata, Paltau. |
| Hydrogenous (supergene-residual weathering by crust (exfiltration): ore lode. | Carbonate: oxide, carbonate-oxide | Goethite (hydrogoethite) – pirolyuzit. | Alicay, Aksay and others. |
| Metamorphic: manganese zone, lens, void. | Terrigenous: oxide | Ferruginous quartzite with manganese minerals. | Amandara, Asman, Dushak, Farish and others. |

## MATERIALS AND METHODS

### *Methods*

*Geological-Genetic Typification of Manganese Occurrences*

Stratiform (syngenetic-sedimentary) manganese ore occurrences (Kazanbulak, Mazar, Gavasai) are controlled by the Upper Eocene-Lower Oligocene littoral deposits of the Paleogene. Carbonate-manganite ores (Figure 1a) are products of the transition from unchanged manganese carbonates to materials of deep oxidation (Figure 1b) with the residues of the original carbonate substance. In the composition of primary-oxide ores, relicts of the initial manganocalcite and manganite are present. The ore is almost completely composed of manganite with insignificant impurities of carbonate and quartz-clay material.

Manganite ores are intermediate products (manganites, pyrolusites and polyperganganite differences) of oxidation of manganocalcites. As a rule, ore material mainly is represented by manganite (Figure 1b) with an admixture of cryptomelane (Figure 1c, d), grains of quartz and clay substance. Rounded cryptomelanic grains consist of concentrically metacolloidal types. The bulk of the manganite is composed of relics of manganocalcite.

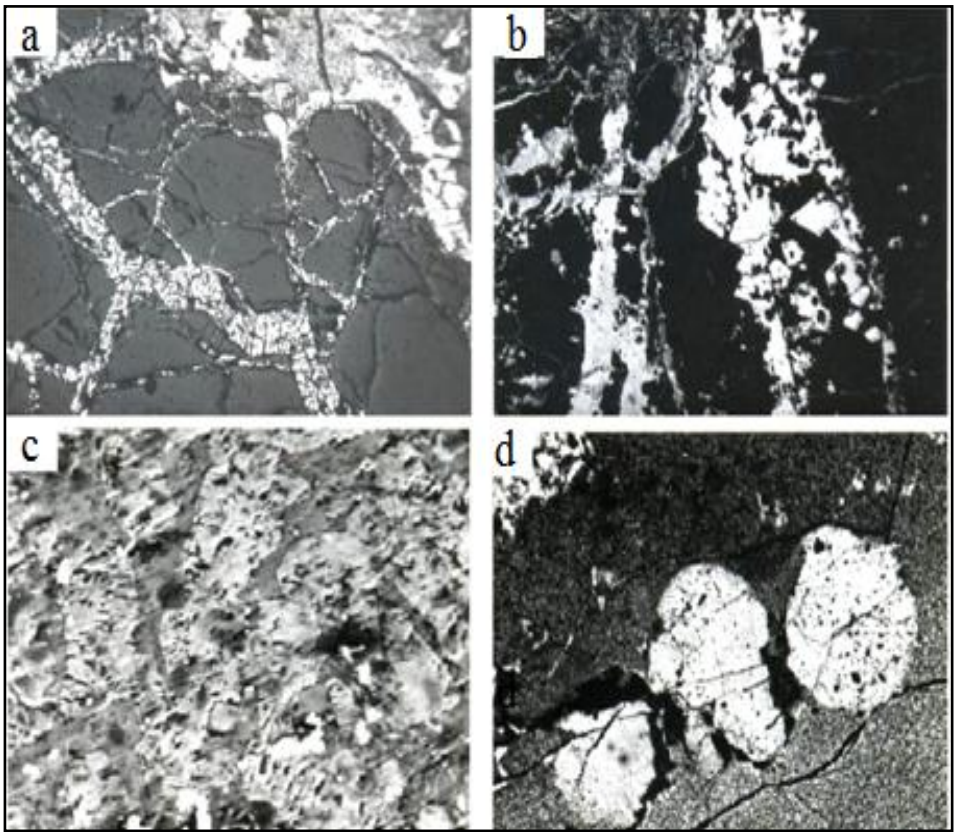


**Figure 1: Manganese Ore, Brecciated Structure; Polished Section, Magnification 40 x; Pseudomorphs of Psilomelan (White) on Manganocalcite (a); Large-Crystalline Pyrolusite (Gray) Fill-up Cracks in Quartz; Pseudomorphs of Psilomelane for Manganocalcite, Polished Section, Occurrence 125 x (b); Manganite Ores of the Occurrence Kazanbulak; Polished Section; Magnification 245 x (c); Fine Crystalline Pyrolusite; Nodular-Shaped Separations of Cryptomelan (Light), Polished Section; Magnification 63 x (d)**

Pyrolusite ores are the final products of oxidation of carbonate-manganite mineral components. Pyrolusite buildups (Figures 2a, b, c, d) consist of insignificant inclusions of manganite, psilomelan, cryptomelan and nsutite. The amount of ore minerals in ore is 29.3%. In clay-marly mass there are concretions (up to

10-15 cm) of pyrolusite. The mineral undergoes crystallization from a colloidal substance, contains relicts of manganite, cryptomelane and others.

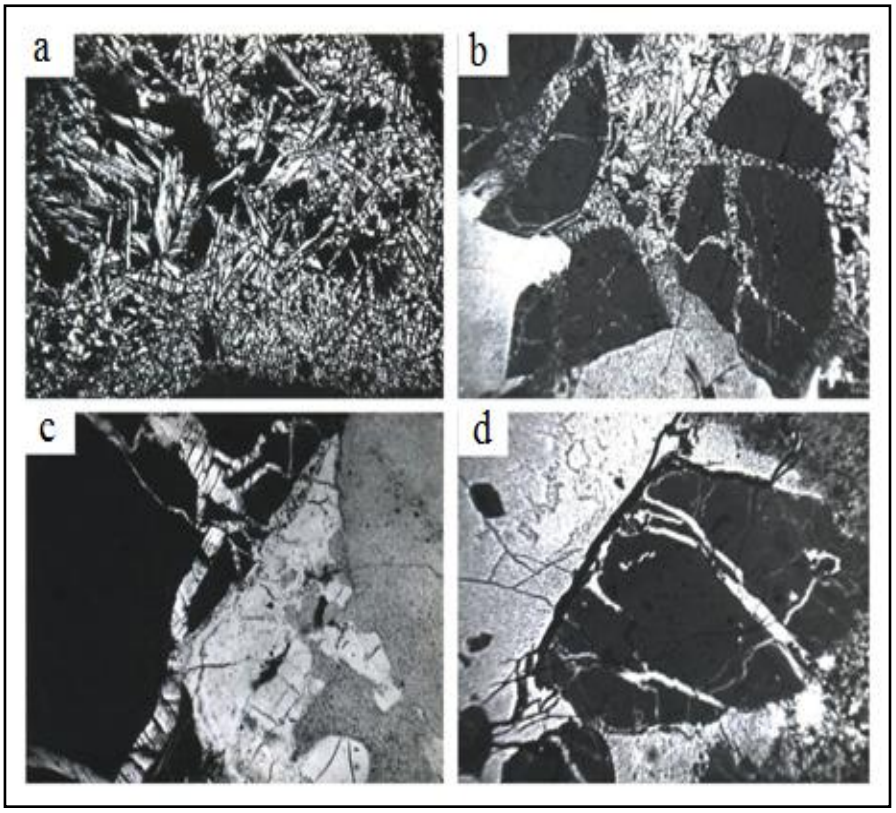


**Figure 2: Pyrolusite Ore, Kazanbulak, Polished Section, Semi-Oxidized Manganese Ore with Geodes from Fossilized Echinoderm Residues with Post Sedimentation Changes, Cavitation in the Middle is made from Large-Crystal Pyrolusite; Magnification 40 x (a); Structure of Substitution by Coarse-Crystalline Pyrolusite; Magnification 40 x (b); Contact of Cryptomelan (White) and Finely Crystalline Pyrolusite (Gray); Cracks in Quartz (Black) are Filled-up by Coarse-Grained Pyrolusite; Magnification 125 x (c); Clastic Material with New Formations (White) of Pyrolusite and Psilomelan; Cracks in the Grain of Quartz are Filled-up by Pyrolusite and Psilomelan, 40 x (d)**

The Mazar (Sattartau) ore occurrence of manganese (Chekunov, 1962) is found in the limestones of the Upper Eocene. The Kazanbulak ore occurrence (located 5-6 km northeast from Mazar) in the littoral (marine) gravel, quartz and spongalite sandstones of the lower Oligocene. The ore occurrences of manganese (Mazar, Kazanbulak, Gavasai) of the Upper Eocene-Lower Oligocene age (oxide composition of ores, littoral formation conditions, etc.) are relatively similar to many deposits in Southern Ukraine (Nikopol), Georgia (Chiatura), Mangyshlak and others.

***Petrographic Features of the Erosion Area***

The source of manganese was the folded basement of the territory (products of high metamorphism, active Upper Paleozoic volcanic-plutonism) as a carrier of increased contents of accessory ore minerals (zircon, apatite, fluorite, minerals of rare earth and REECe + Y, U, Th, etc.) in humid climate (Paleocene-Eocene), undergoing intensive chemical weathering.

Magmatic formations (Rafikov, 2012) trachybasalt-trachyandesite-rhyolites, $D_1$ (plutonic analogs - gabbro-monzonite-syenite complex), trachybasalt-trachytes, $C_1$ (gabbro-peridotite-anorthosites and gabbro-monzonite-syenites), trachybasalt-trachyandesite- trachydacites, $C_2$ and trachyandesite-dacites, $C_2$ (gabbro-monzodiorite-granodiorites), rhyolite-trachyriolites, $P_1$ (granite-leucogranites), trachybasalts, $P_{1sh}$

(gabbro-monzonite-syenites) are also geochemically specialized on Mn. Rock-forming biotites, amphiboles, pyroxenes, as well as accessory magnetite, ilmenite, sphene and other minerals are carriers of associated manganese (Yusupov, 1983). Manganese during the weathering process is released, accumulating in a weakly acidic and acidic weathering crust (secondary minerals Mn - vernadite, psilomelan, cryptomelan, manganocalcite, etc.) are formed.

The mechanism of Mn separation from Fe during the formation of littoral ore deposits occurs in catchments (Strakhov *et al*., 1968), on the developed weathering crust, accompanied by feeding of ore areas with sedimentary material. According to known provisions (Roy, 1986, Strakhov *et al*., 1968), V.I. Popov, V.I. Troitsky, N.A. Shilo (2000), in different types of rocks there is a stratification of ore matter. In zones with active hydrodynamic regimes, the ore material precipitates forms a cluster of facies (Au, Zr, Ti, Cr, etc.) at the base of facial rhythms, another group of elements with the active participation of organic matter (Mo, Re, Sc, V, etc.) in free form, is concentrated in reducing conditions. According to V.I. Troitsky, the migratory series of deposits of the open sea and the coast is represented in the following form: [Ti, V, Zr] → [Ba, Cr, Pb, Ga] → [Ni, Cu] → [Mn] → [Sr].

The chemical and mineral composition of the manganese ore occurrences of Kazanbulak (Table 2). In the initial ore, the mass fraction of manganese accounts for 18.3%. Ore minerals - pyrolusite, manganite, cryptomelan, psilomelan, manganocalcite, etc. The average amount of ore minerals is 29.3%. The peroxide ratio ($MnO_2$ / Mn) is 1.51 - the index of the oxide content of the mineral components of the concentrate, which is in accordance with the requirements for manganese ore (Chiatura, Nikopol, Ukraine).

**Table 2: The Chemical Composition of Manganese Ore %**

| | **Qazanbulaq** | | | | | **Mazar (Chekunov, 1962)** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **4/1** | **4/2** | **4/3** | **4/4** | **average** | **61** | **62** | **63** | **Average** |
| $SiO_2$ | 8.80 | 10.50 | 19.10 | 15.00 | 13.35 | 3.4 | 8.14 | 14.60 | 8.71 |
| $Al_2O_3$ | 4.50 | 5.40 | 3.60 | 3.50 | 4.25 | 0.70 | 2.20 | 2.00 | 1.63 |
| $Fe_2O_3$ | 1.77 | 2.11 | 2.50 | 2.38 | 2.19 | 1.00 | 0.30 | 1.86 | 1.05 |
| $MnO_2$ | 72.80 | 68.70 | 57.60 | 66.00 | 66.28 | | | | |
| MnO | - | 0.10 | 0.20 | 0.80 | 0.28 | | | | |
| CaO | 3.40 | 3.10 | 3.50 | 3.40 | 3.35 | 44.03 | 25.54 | 4.48 | |
| MgO | 0.74 | 0.82 | 0.86 | 0.85 | 0.82 | | | | |
| BaO | 0.01 | 0.01 | 0.02 | 0.02 | 0.02 | | | | |
| $K_2O$ | 1.12 | 1.14 | 1.27 | 1.29 | 1.21 | | | | |
| $Na_2O$ | 0.44 | 0.47 | 0.64 | 0.58 | 0.53 | | | | |
| $P_2O_5$ | 0.02 | 0.10 | 0.08 | 0.09 | 0.07 | 0.045 | | 0.182 | 0.076 |
| $CO_2$ | 2.70 | 2.90 | 3.40 | 3.10 | 3.03 | | | | |
| $H_2O^{\pm}$ | 1.16 | 2.07 | 4.01 | 1.17 | 2.10 | | | | |
| ППП | 2.10 | 2.70 | 3.10 | 2.10 | 2.5 | | | | |
| **Total** | **99.56** | **100.12** | **99.88** | **100.28** | **99.98** | | | | |
| Mn | 46.00 | 43.50 | 36.50 | 42.30 | 42.07 | 12.00 | 20.65 | 40.74 | 24.46 |
| Fe | 1.24 | 1.48 | 1.75 | 1.67 | 1.54 | 0.70 | 0.20 | 1.30 | 0.73 |
| P | 0.009 | 0.043 | 0.08 | 0.039 | 0.042 | 0.020 | | 0.080 | 0.05 |
| S | - | 0.001 | 0.003 | 0.002 | 0.002 | 0.030 | | 0.030 | 0.03 |

In the compositions of primary manganese ores, platinum metals are also present. Heavy deficit for the production of high-grade concentrates of peroxide (oxide) manganese ores, intensive extraction of them in neighboring countries (Georgia, Ukraine, Kazakhstan, etc.), in the future there is a need to develop ore

occurrences of manganese Kazanbulak and Mazar with the extraction (along with manganese) additional) metals (Tables 3, 4), (Abdumuminov, 2015).

**Table 3: Oxide Manganese Ore: Impurity Elements; g/t (ICP-MS Analysis, the State Enterprise "Central Laboratory")**

| Elements | Oxide Manganese Ore (Sample Number). g/t | | | | | |
|---|---|---|---|---|---|---|
| | 1-Кк | 2-Кк | 3-Кк | 4-Кк | 5-Кк | $X_{zk}$ |
| Au | 0.60 | 0.50 | 0.50 | 0.20 | 0.30 | 0.0043 |
| Ag | 80.30 | 0.50 | 0.70 | 1.40 | 0.10 | 0.07 |
| Pd | 2.30 | 1.10 | 0.30 | 0.10 | 0.10 | 0.013 |
| Pt | 0.005 | 0.005 | 0.002 | 0.011 | 0.003 | 0.005 |
| Pb | 3070 | 124 | 524 | 3511 | 39 | 16.0 |
| Zn | 3585 | 145 | 1338 | 108258 | 315 | 83.0 |
| Cu | 3122.9 | 18.6 | 70.5 | 4.7 | 24.8 | 47.0 |
| Mo | 55.2 | 14.4 | 13.2 | 6.0 | 13.5 | 1.1 |
| Re | 0.004 | 0.038 | 0.004 | 0.002 | 0.002 | 0.0008 |
| Bi | 3.88 | 0.62 | 0.48 | 0.32 | 0.72 | 0.009 |
| In | 4.72 | 0.06 | 0.09 | <0.001 | 0.05 | 0.25 |
| Tl | 3.88 | 5.21 | 0.78 | 0.60 | 0.19 | 1.00 |
| Ga | 15.40 | 19.20 | 23.20 | 4.50 | 27.50 | 19.0 |
| Se | 3.91 | 3.66 | 2.58 | 3.56 | 2.60 | 0.05 |
| Te | 0.057 | 0.074 | 0.131 | 0.290 | 0.051 | 0.001 |
| Cr | 28.2 | 30.0 | 25.7 | 5709.2 | 159.1 | 83 |
| Co | 7.2 | 6.5 | 15.1 | 398.4 | 16.7 | 18 |
| Ni | 9.17 | 8.37 | 6.20 | 198.4 | 5.6 | 58 |
| V | 56.10 | 31.60 | 26.10 | <0.001 | 36.3 | 90 |
| Nb | 2.62 | 9.64 | 1.15 | 5.03 | 0.17 | 20 |
| Ta | 0.21 | 1.10 | 0.22 | 0.33 | 0.02 | 2.5 |
| W | 16.80 | 8308.8 | 151.1 | 16.4 | 29.40 | 1.3 |
| Sn | 6.30 | 3.02 | 0.54 | 44.73 | 0.38 | 2.5 |
| Be | 2.39 | 9.98 | 33.25 | 0.15 | 3.99 | 3.8 |
| Li | 15.90 | 41.00 | 375.40 | 10.30 | 4.60 | 32.0 |
| B | 37.0 | 18.0 | 32.0 | 1640 | 99.0 | 12.0 |
| As | 111.0 | 58.0 | 567.0 | 52.0 | 154.0 | 1.7 |
| Sb | 11.5 | 1.7 | 1054.6 | 26.7 | 871.9 | 0.5 |
| Rb | 118.4 | 165.9 | 81.0 | 6.0 | 12.4 | 200 |
| Cs | 12.0 | 1896.4 | 21.1 | 1.1 | 1.0 | 6.0 |

*Note: Sample 1-Kk (Qazanbulaq, Kurama zone), 2-Ik (Issyk-Kul, the Tien-Shan), ore subplatform-sedimentary (stratiform- singenitic-diagenetic) verhneotsen-Lower Oligocene; 3-Kk (Dautash, Uzbekistan), 4 and 5-Kk-Kk (Gvettara, Sahara, Algeria) - volcanic-sedimentary (metamorphogenic); Xzk (average content in the earth's crust, according to A.P. Vinogradov)*

**Table 4: Rare Earth Elements Yttrium, Scandium, Thorium, Uranium and Manganese in Oxide Ores, g/t (ICP-MS Analysis, the State Enterprise "Central Laboratory of the State Geology Committee of Uzbekistan")**

| Elements | Oxide manganese ore. g / t | | | | | The earth's crust and its shell | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1-Кк | 2-Ік | 3-Кк | 4-Кк | 5-Кк | I | II | III | IV |
| ***Ce*** | | | | | | | | | |
| La | 85.6 | 103.3 | 24.4 | 2.3 | 10.6 | 14.5 | 16.0 | 16.6 | 14.2 |
| Ce | 79.7 | 83.0 | 36.1 | 5.7 | 7.0 | 28.2 | 30.0 | 30.4 | 28.4 |
| Pr | 1.9 | 28.1 | 5.1 | 1.3 | 2.3 | 4.1 | 4.6 | 5.2 | 4.8 |
| Nd | 71.4 | 89.9 | 19.4 | 3.6 | 7.9 | 15.5 | 17.0 | 16.6 | 16.4 |
| Sm | 16.8 | 18.9 | 4.0 | 0.7 | 1.4 | 3.8 | 4.0 | 3.9 | 4.2 |
| ***Tb*** | | | | | | | | | |
| Eu | 4.92 | 7.32 | 4.4 | .30 | 0.43 | 1.2 | 5.3 | - | - |
| Gd | 15.9 | 19.2 | 4.00 | 0.80 | 1.30 | 3.80 | - | 5.50 | 5.00 |
| Tb | 2.98 | 2.41 | 0.52 | 0.12 | 0.20 | - | - | - | - |
| *Er* | | | | | | | | | |
| Dy | 19.51 | 13.07 | 3.15 | 0.82 | 1.16 | 3.50 | 3.60 | 3.70 | 4.30 |
| Ho | 3.93 | 2.34 | 0.57 | 0.17 | 0.23 | - | - | - | - |
| Er | 11.09 | 6.23 | 1.61 | 0.46 | 0.61 | 2.4 | 2.2 | 2.00 | 2.20 |
| Tm | 1.64 | 0.82 | 0.22 | 0.08 | 0.09 | - | - | - | - |
| ***Yb*** | | | | | | | | | |
| Yb | 12.21 | 5.82 | 0.28 | 0.07 | 0.09 | - | - | - | - |
| Lu | 1.65 | 0.88 | 0.07 | 0.09 | 0.88 | - | - | - | - |
| Y | 169.50 | 91.80 | 23.00 | 4.60 | 6.70 | 20.90 | 17.00 | 14.80 | 18.50 |
| Sc | 11.17 | 5.99 | 3.49 | 2.87 | 1.55 | 10.00 | - | 3.00 | 24.00 |
| U | 121.84 | 20.68 | 49.50 | 1.01 | 18.69 | 3.00 | 2.50 | 3.5 | 0.50 |
| Th | 15.33 | 22.60 | 2.37 | 1.53 | 2.36 | 13.00 | - | 18.00 | 3.00 |
| **Total** | | | | | | | | | |
| $REE_{Ce+Y}$ | 329.03 | 381.29 | 105.43 | 16.83 | 33.91 | 77.00 | 93.80 | 83.90 | 79.50 |
| $REE_{Ce}$ | 255.20 | 323.52 | 89.00 | 13.60 | 29.20 | 66.10 | 82.70 | 72.71 | 68.00 |
| $REE_{Y}$ | 73.83 | 57.77 | 16.43 | 3.23 | 4.71 | 10.90 | 11.10 | 11.20 | 11.50 |
| $REE_{Y}$+Y | 243.33 | 149.57 | 39.93 | 7.83 | 11.41 | 31.80 | 28.00 | 26.10 | 30.00 |
| $REE_{Ce+Y}$+Y | 498.53 | 473.53 | 128.43 | 21.43 | 40.61 | 97.00 | 110.80 | 98.70 | 98.00 |
| $REE_{Ce}/REE_{Y}$+Y | 1.0 | 2.2 | 2.3 | 1.7 | 2.6 | 2.1 | 3.0 | 2.8 | 2.3 |

Sample number: 1 Kk (Qazanbulaq deposit Kurama zone), 2-Ik (Issyk-Kul, the Tien-Shan), ore subplatform-sedimentary (stratiform-singenetic-diagenetic) Upper Eocene-Lower eocene, 3-Kk (Dautash, Uzbekistan), 4- kk and kk 5 (Gvettara, Sahara) - volcanic-sedimentary (metamorphogenic).

The noble (Au, Ag, Pt, Pd), non-ferrous (Cu, Pb, Zn, Mo, etc.) and other strategic metals (Nb, Ta, Sn, Bi, Be, Li, etc.) accumulated in the oxide manganese ores, rare earth elements, yttrium, scandium, uranium and thorium. The amount of REECe + Y + Y (Table 3) in the composition of the Kazanbulak (Kurama ridge) ore is 498.53 g / t (in terms of the oxide composition 1500 g / t). In ores, the intensity of the concentration of noble, non-ferrous and other strategic metals (rare elements, rare earths, yttrium, uranium, etc.) is associated with an increase in the content of organic matter in which strategic metals accumulated (Cu, Mo, Re, REECe + Y + Y, U, Th, etc.) of sorption type:

Qazanbulaq (Uzbekistan): [Ag, Pd, Pb – Bi, Cd] – [Au, Se, Te] – (Cu, Mo, Re) – (Co, As, Sb – U – Zn. In) – W, Sn – Tl, Ga, B – Be, Li, Th – Cr, Ni, V – Nb, Ta.

Issyk-Kul (Kyrgyzstan): [Au, Pd, W, Bi, As] – (Te, Tl, Re, Se) – (Pb, Zn, Ag, Cd) – Sb – (Ta, Nb, Sn, Be, Li) – (Cr, V, Ni, Co) – Cu, Zn.

| | |
|---|---|
| Gvetara | [Au] – (Bi, As, Sb) – (Te, Se) – Be, Li, W, Mo, Re – B – |
| (Sahara, Algeria): | Pd, Ag, Pb, Zn, Cd, In, Tl – Cr, Cu, Co, V, Ni – Be, Li, Ni, Ta, Ga. |
| Dautash | [Au, W] – (As, Sb) – Be, Te, Se – Pt, Cu, Sn, Te, In, Ga – |
| (Uzbekistan): | Cr, V, Ni, Co – Zn – Ta, Nb. |

The rare-earth nature of manganese oxide ores by the elements of Ce- and Y-land (REECe / REEY + Y = 1.00) is practically similar: Ce-earths (La, Ce, Pr, Nd, Sm, Eu) in deposits of volcanogenic-sedimentary (metamorphosed) geological-genetic type (Gwetthara, Bukais, Dautash) are in increased amounts relative to the elements of the Y-associations.

***Conclusion***

The Upper Eocene-Lower Oligocene primary-sedimentary manganese ores of the Chatkal-Kurama zone are of considerable interest in the study of associated ore and non-metallic impurity elements in them.

Manganese ore mineralization (Kazanbulak, Gavasay, Mazar, etc.) of the Upper Eocene-Lower Oligocene are found on Upper Paleozoic rocks - volcanic-plutonic complexes $C_2$, $C_{2-3}$, P-$T_1$. Carbonate and oxide-carbonate ores (Mazar) are interchanged by oxide (Kazanbulak) from the higher oxides of manganese

The intensity of accumulation of strategic chemical elements in oxide manganese ores is associated with the processes of differentiation of ore matter. In the humid and developed parts of the sections (Kazanbulak, Mazar, Gavasai, etc.), are formed in complex with organic matter impurity sets of strategic chemical elements of the sorption type (Cu, Mo, Re, Nb, Ta, Be, $REE_{Ce + Y}$ + Y, U and other). The Upper Eocene-Lower Oligocene formations of the Chatkal-Kurama zone (littoral coastal-marine with sedimentary types of manganese ores) are promising for a complex of rare-earth elements, uranium, cesium, etc.

Ore minerals of manganese (pyrolusite, cryptomelan, etc.) are enriched in cerium soils, yttrium earths are in a dispersion state. Occurrence form of REE elements are finely impurity (nanostructured). In Mn minerals REE concentrations occurs synchronously with U, Th and others.

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