# Mineralogy of Nb–Ta bearing apatite–cordierite metasomatised metabasite from Mostovyi ore occurrence (Ukrainian Shield)

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**Abstract:** The unique type of rare-metal metasomatite from the Mostovyi Ta–Nb–Au ore occurrence at the western margin of Korsun–Novomyrgorodskyi pluton is described. Nb–Ta-bearing metasomatite was formed in a result of alteration of metabasite rocks by P-, F-rich fluid from felsic magmas. The main characteristic and chemical compositions of main and secondary minerals in metasomatite and metabasite are shown.

## Introduction

The Mostovyi ore occurrence located in the northern part of the Bratsk–Zvenygorod tectonic structure at the western margin of Korsun–Novomyrgorodskyi pluton within the Ingul Megablock of the Ukrainian Shield (Kropyvnytskyi region, central part of Ukraine) (Fig. 1). The Mostovyi occurrence composed of Proterozoic gneisses of Ingul series intruded by granite and pegmatite of Kirovagrad complex. The ore mineralization presented by Au and rare metal (Ta, Nb) elements. Gold is in relationship to graphite-bearing gneisses and rare metal- to aplitic-pegmatites and metasomatites (Bezvynnyi 2005; Ivanov et al. 2011). The contribution describes the Nb–Ta-bearing apatite–cordierite metasomatite (ACM) from Mostovyi Au-rare metal occurrence.

All samples were selected from exploration borehole of the Mostovyi occurrence. Thin sections were studied in reflected light. The major-element has been analysed by JEOL JXA-8520F. Analytical results in empirical formulaes of minerals from ACM and metabasite are given in Table 1.

## Petrography

Host metamorphic rocks are presented by graphite–cordierite–biotite, graphite–biotite, biotite–muscovite gneisses and mylonites. Magmatic rocks are represented by aplite, pegmatites and granite but graphite–cordierite–biotite gneisses dominate. They are grey, dark grey with schistosity structure, commonly equigranular, less porphyroblastic. Porphyroblasts are represented by cordierite and K-feldspar, 3–8 mm in size. Groundmass is fine- to medium-grained. The main minerals: biotite, cordierite, plagioclase, quartz, K-feldspar, graphite; accessory minerals are zircon, monazite, apatite, sillimanite.

Rare metal apatite–cordierite metasomatite hosted by porphyroblastic biotite–cordierite gneisses and contain small relic of metabasite rocks. The wide of metasomatic zone is about 3 meters. The main minerals form two size group: first presented by tabular cordierite, 3 to 15 mm in size; second — grains groundmass in

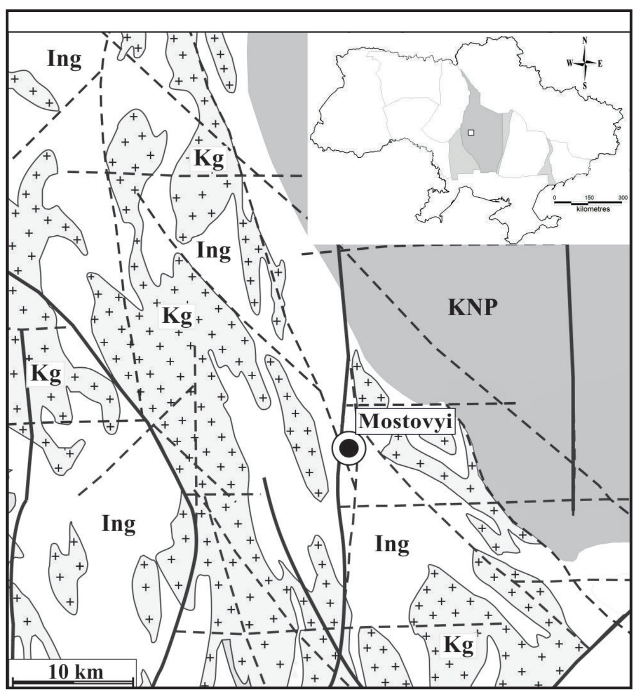


**Fig. 1.** Location of Mostovyi Nb–Au ore occurrence. KNP — Korsun–Novomyrgorodskyi pluton, Kg — granitoids of Kirovograd complex (S-type), Ing — gneisses of Ingul series.

interstitial of cordierite and consists of smaller cordierite, apatite, quartz, sulphides, graphite and biotite (0.4–1.3 mm). Mineral composition ACM in vol. %: cordierite 60–85, apatite 10–30, biotite 3–10, quartz 1–7, graphite 2–5, tourmaline (identified in thin-section) 0–2, small pyroxene relic. Sulphides and sulfosalts are represented by pyrrhotite (3–5 %), arsenopyrite, lollingite, pyrite, chalcopyrite and less molybdenite. Oxides are represented by Nb-rutile and relics of ilmenite. Group of orthophosphate is formed by graftonite, sarcopside, jahnsomervellite. Secondary minerals are chlorite, carbonate (sometimes up to wt. 3 %), hematite, and phosphate (arrojadite, ludlamite, laudite). Accessories: monazite, zircon, sillimanite, rarely uraninite.

Relics of metabasite bodies are represented by transitional rock type from gabrodiorite to gabbro–norite, groundmass is medium-grained (1.2–2.2 mm). Mineral composition in vol. %: hornblende 45–50, plagioclase 25–30, salite 10–15, biotite 5–6, orthopyroxene 2–3, titanite about 1, ilmenite <1 %. Among accessories is only apatite.

## Mineralogy

### *Nb–Ta bearing apatite-cordierite metasomatite*

Light-blue **cordierite** forms tabular grains from 0.5 to 15 mm in size, with numerous inclusions of apatite, quartz, biotite, graphite, Nb-rutile, sulphides, monazite, zircon. The chemical composition of the mineral phases is similar. Cordierite grains are mostly magnesian, Fe/(Fe+Mg value is 0.3–0.4 and gradually increase from the core to rime. Al varies from 3.88 to 3.98 apfu. Cordierite is partly transformed to pinnite aggregates. In transitional phase cordierite is hydrated and enriched in iron. Brown **biotite** forms singular euhedral grains <2 mm in size, or small aggregates up to 4 mm. Chemical composition is homogeneous, average Fe/(Fe+Mg) value is 53.8 at. %, annite end-membership is dominant, $TiO_2$ varied in narrow range 2.14–2.88 wt. %, fluorine content is very low. **Sillimanite** is presented in very fine needles (0.1–0.5 mm) included in cordierite and prismatic crystals (<0.2 mm) in groundmass, poor at trace elements. **Graphite** occurs as non-oriented fine-flakes, less than 0.5 mm in size or aggregates included in quartz, forms intergrowth with biotite, sulfides and arrojadite. **Quartz** forms small rounded grains in groundmass, commonly with numerous graphite inclusions.

**Nb-rutile** commonly occurs as inclusions in cordierite and rarely in apatite, and singular grains in groundmass

**Table 1:** Empirical formulas of investigated minerals.

| | |
|---|---|
| **Apatite-cordierite metasomatite** | |
| ***Silicate*** | |
| Cordierite | $(Na_{0.166–0.18}K_{0.001})_{0.174}(Mn_{0.049–0.053}Fe^{2+}_{0.58–0.652}Mg_{1.195–1.227})_{1.89–1.92}[(Fe^{3+}_{0.1–0.116}Al_{3.88–3.98})_4Si_{5.04–5.056}O_{18}]$ |
| Titanite | $(Ca_{1.0}LREEY_{0.002})_{1.0}(Sn_{0.003}Al_{0.16}Ti_{0.78})_{0.95}[Al_{0.01}Si_{0.99}O_4](F_{0.16}O_{0.84})_{1.0}$ |
| Biotite | $(Na_{0.026}K_{1.776})_{1.802}(Ti_{0.291}Cr_{0.036}Fe_{2.44}M\ g_{2.094}Al_{0.733})_{5.63}[(Al_{2.544}\ Si_{5.456})_2O_{20}](OH)_2$ |
| Sillimanite | $Al^{vi}_{2.002}\ [(Al^{iv}_{0.011}Si_{0.989})_{1.0}O_5]$ |
| ***Oxides*** | |
| Nb-Rutile | (1) $(W_{0.001}V_{0.011}Cr_{0.06}Fe_{0.035}Ta_{0.014}Nb_{0.074}Ti_{0.855})_{0.999}O_2$<br>(2) $(W_{0.0}V_{0.016}Cr_{0.008}Fe_{0.046}Ta_{0.03}Nb_{0.088}Ti_{0.809})_{0.998}O_2$<br>(3) $(W_{0.001}V_{0.016}Cr_{0.009}Fe_{0.064}Ta_{0.045}Nb_{0.108}Ti_{0.755})_{0.99}O_2$ |
| ***Sulfide and sulfosalts*** | |
| Pyrrhotite | $Fe_{0.921}Ni_{0.003}Co_{0.002}As_{0.001}S_{1.073}$ |
| Pyrite | $Fe_{0.999}Ni_{0.007}Co_{0.001}S_{1.993}$ |
| Arsenopyrite | $Fe_{0.763–1.004}Ni_{0.01–0.167}Co_{0.006–0.075}As_{1.054–1.156}S_{0.827–0.911}$ |
| Lollingite | $Fe_{0.747}Ni_{0.17}Co_{0.103}As_{1.934}S_{0.043}$ |
| Molybdenite | $MoS_2$ |
| ***Phosphate minerals*** | |
| Apatite | $(Ca_{4.681}Mn_{0.109}Fe_{0.042})_{4.832}\ (PO_4)_3(F_{0.785}OH_{0.215})_{1.0}$ |
| Monazite-(Ce) | $Ca_{0.081}\ Th_{0.017–0.104}Ce_{0.396}\ La_{0.212}\ Nd_{0.137}Sm_{0.013}\ P_{1.0}O_4$ |
| Graftonite | $(Mg_{0.307}Mn_{0.700}Ca_{0.738}Fe_{1.152})_{2.903}(PO_4)_2$. |
| Sarcopside | $(Mn_{0.239}Mg_{0.991}Fe_{1.607})_{2.853}(PO_4)_2$. |
| Jahnsomervellite | $Na_{3.886}Ca_{3.247}Al_{0.065}Ba_{0.008}Sr_{0.004})_{7.189}(Mg_{8.933}\ Fe_{7.577}\ Mn_{3.523}\ Zn_{0.076}Sc_{0.047})_{20.49}(P_{17.88}Si_{0.11}O_{72})$ |
| Ludlamite | $(Fe_{3.608}Mg_{1.517}Mn_{0.222})_{2.781}(PO_4)_2x\ nH_2O$ |
| Arrojadite? | $(Ca_{0.165}Fe_{0.092}Mg_{0.898}Mn_{0.008})_{2.835}Al_{1.821}(P_{11.987}Si_{0.11}O_{48})(OH_{1.865}F_{0.13})_2$ |
| Lazulite | $(Na_{3.679}K_{0.523}Ca_{0.294}Ba_{0.899}Sr_{0.016}Pb_{0.002})_{5.41}(Fe_{3.608}Mg_{4.567}Mn_{4.643})_{12.818}Al_{0.948}(P_{1.86}Si_{0.138}O)_4$ |
| **Metabasite** | |
| Hornblende | $(Ca_{1.939}Na_{0.163}\ K_{0.054})_{2.161}(Cr_{0.006}Ti_{0.042}Mn_{0.124}Fe_{1.986}Mg_{2.58}Al^{vi}_{0.262})_{5.006}[(Al^{iv}_{0.863}Si_{7.137})O_{22}]\ (Cl_{0.001}F_{0.238}OH_{1.761})_{2.0}$ |
| Salite | $Ca_{0.967}\ (Fe_{0.44}Mg_{0.566}\ Mn_{0.013})_{1.029}\ Al_{0.024}\ (Al^{vi}_{0.032}\ Si_{1.976}O_6)$ |
| Titanite | $(Ca_{1.0}LREEY_{0.002})_{1.0}(Sn_{0.003–0.012}Al_{0.17}Ti_{0.78})_{0.96}Si_{0.99}O_4(F_{0.16}O_{0.84})_{1.0}$ |
| Apatite | $(Ca_{4.743}\ Mn_{0.106}\ Fe_{0.043})_{4.892}\ (PO_4)_3\ (F_{0.852}\ OH_{0.148})_{1.0}$ |
| Ilmenite | $Fe^{2+}_{0.874}\ Fe^{3+}_{0.052}\ Mn_{0.075}Ti_{0.97}\ O_4$ |

(Fig. 2). The lowest Nb–Ta content shows rutile from apatite ($Nb_2O_5$ 10.47–11.94 wt. %, $Ta_2O_5$ 2.24–4.76 wt. %) (1). Ta–Nb content in rutile from groundmass is slightly higher ($Nb_2O_5$ 12.09–13.20 wt. %, $Ta_2O_5$ 6.28–8.56 wt. %) (2). The richest Nb–Ta content exhibit rutiles included in cordierite ($Nb_2O_5$ — 13.82–16.10 wt. %, $Ta_2O_5$ — 9.45–11.49 wt. %) (3) (Fig. 3, Table 1). Also, rutile slightly enriched in $V_2O_3$ 2.03–3.35 wt. % and $Cr_2O_3$ 0.978–2.03 wt. %. The lowest content of these oxides is in rutile of type (1). Relic of **ilmenite** was identified on the very thin (<1 μm) rime of sulphides grains.

*Sulphides*

**Pyrrhotite** is the most common sulphide mineral in ACM. It was identified in groundmass in association with chalcopyrite and sphalerite. **Pyrite** replaces pyrrhotite, fills the thin fissure in groundmass and rarely is replaced by hematite. **Arsenopyrite** is in association with pyrite, lollingite and graphite. Internal zoning of arsenopyrite is caused by uneven content of Co and Ni. **Lollingite** is closely associated with arsenopyrite. It forms anhedral grains in groundmass or prismatic grains included in cordierite. Replacement of lollingite by arsenopyrite was also observed. Lollingite shows high content of Co 2.79–3.17 wt. % and Ni 4.82–5.05 wt. %. **Molybdenite** is rare mineral occurring in intergrowth with graphite.

*Phosphates*

**Fluorapatite.** Greenish fluorapatite in ACM forms rounded grains 0.2–2 mm in size and situated in interstitial of cordierite grains. Colourless fluorapatite from

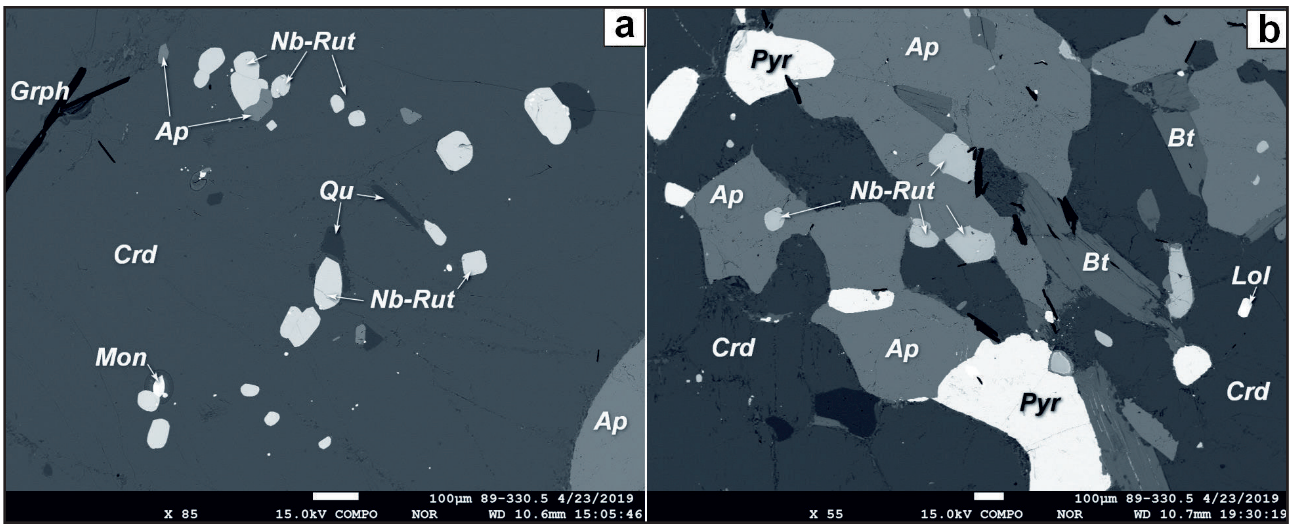


**Fig. 2.** BSE micrographs: **a** —Nb-rutile inclusions in cordierite; **b** — Nb-rutile in interstitial groundmass and as inclusions in apatite.

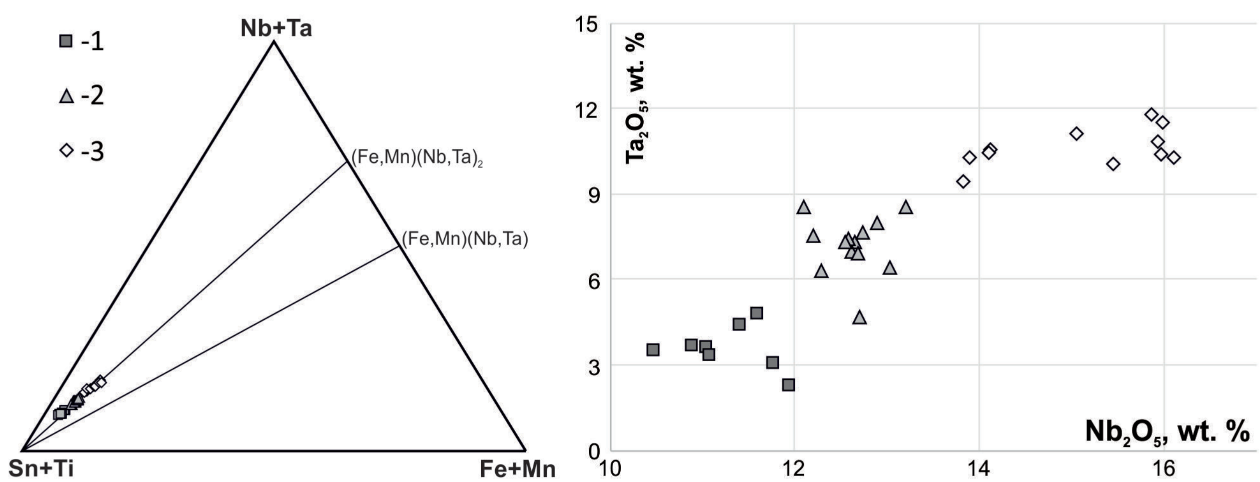


**Fig. 3.** Chemical composition of Nb-rutile from: 1 — inclusions in apatite, 2 — single grains in groundmass, 3 — inclusions in cordierite.

host gneisses forms very fine grains (<50–70 μm), shows the highest fluorine (up to 4.37 wt. %) and the lowest Mn, Fe (Mn/Fe<1) contents, and very low REE content. Apatite from ACM shows a bit lower content of fluorine (2.7 to 3.4 wt. %), and significantly higher MnO and FeO (Mn/Fe>2). Total content of LREE is <0.22 wt. %.

Secondary phosphates form aggregates, 0.4–2.0 mm in size, consist of graftonite, fine grains phosphates of fillowite group, arrojadite, lazulit and veins of ludlamite. **Graftonite** ($X_{Fe}$=0.54) forms tabular grains <0.5 mm in size and it is the most common orthophosphate. Graftonite is Mn-enriched ($X_{Mn}$=0.32) and Mg-rich ($X_{Mg}$=0.14). **Sarcopside** occurs in intergrowth with apatite, where apatite in such case very similar to quartz myrmekite in plagioclase. The size of this aggregates very variable, but less than 0.5 mm. Sarcopside is distinctly Fe-dominant ($X_{Fe}$=0.57), Mg-enriched ($X_{Mg}$=0.35) and Mn-poor ($X_{Mn}$=0.08). Orthophospate of **fillowite** group is rare, form small single tabular grains, 5–30 μm in size. According to classification diagram (Grew et al. 2010), plot points of fillowite group orthohosphate are placed on the border between jahnsomervellite and chladnite fields, but last membership is slightly predominant. They are slightly Mg-dominant ($X_{Mg}$=0.45), Fe-enriched ($X_{Fe}$=0.38) and Mn-rich ($X_{Mn}$=0.18).

Arrojadite, lazulite and ludlamite occur within phosphate aggregate as well as the single grains but in accessory amount. **Ludlamite** is the most common of that group, forms very fine (up to 5–7 μm) alternating veins within sarcopside grains. **Arrojadite** (?) is rare mineral which occurs in intergrowth with graphite or on the rime of phosphate aggregate <15 μm in size. **Lazulite** is in a small grain on the contact between graftonite and cordierite, formed as a result from cordierite alteration.

**Monazite-(Ce)** is present in a singular tabular grains (<200 μm in size) or as intergrowth with apatite. The content of $ThO_2$ and $UO_2$ varies from 1.9 to 11.6 wt. % and from 1.5 to 3.5 wt. % respectively. Such distribution of Th and U caused patchy and zonal internal structure. The content of CaO is 1.25–2.25 wt. % in a Th poor grains, and up to 3.5 wt. % in Th rich. Introduction Th and Ca in structure monazite are provides by brabantite substitution scheme ($X_{brb}$— 0.1–0.3).

### *Mineralogy of metabasite rocks*

A**mphibole** occurs in prismatic grains (0.5–2.0 mm in size) and presented by magnesiohornblende (f — 44.6 at. %). Concentration of Zn, Ni, Sr is less than 0.05 wt. %. **Titanite** forms singular grains (<300 μm) or small aggregate. Heterogenic internal structure is caused by the different content of $SnO_2$ (0.39–1.1 wt. %.). **Salite** was identified as a relic anhedral grains, 100–150 μm in size, included in hornblende. The Fe/(Fe+Mg) value is 42.9–44.7 at. %. Content of $Al_2O_3$ less than 0.8 wt. % and content of Na, Zn is <0.07 wt. %. **Ilmenite** appears as a small inclusion in titanite, less than <10 μm in size. Ilmenite enriched in MnO — 1.7–4.0 wt. %).

## Discussion and conclusion

The Nb–Ta-bearing apatite-cordierite metasomatite is a new type or rare metal mineralisation at the western margin of Korsun–Novomyrgorodskyi pluton. The origin of Nb–Ta mineralisation is still unclear. We can conclud that rare metal metasomatite was formed in a result of strong hydrotermal-metasomatic alteration of metabasite rocks by postmagmatic fluid enriched in F, P (and probably Ta–Nb) in conditions of amphibolite facies of regional metamorphism. The sources of postmagmatic fluids were numerouse rare-metal granitoids dykes intruded gneisses.

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## References

Bezvynnyi V.P. 2005: Rare metal, gold mineralization and metasomatic processes of the Petroostriv ore field. *Scientific proceedings of UkrSGRI* 1, 82–84 (in Ukrainian).

Ivanov B.N., Kosuga V.N. & Pogukai V.I. 2011: Areal and exocontact rare metal metasomatites Shpolano-Tashlyk ore region. *Geochem. and Ore Form.* 30, 10–17 (in Russian).

Grew E., Yates M., Beane R., Floss C. & Gerbi C. 2010: Chopinite-sarcopside solid solution, $[(Mg,Fe)_3\square](PO_4)_2$, in GRA95209, a transitional acapulcoite: Implications for phosphate genesis in meteorites. *American Mineralogist*, 95, 260–272.