High REE and Y Concentrations in Mo-Au Ores of the Kis-Kuel IOCG Deposit, East Yakutia (Russia)

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Abstract. This paper presents the results of an updated from 2008-2019 study of the Kis-Kuel promising area and is devoted to the discovered unusual molybdenite + gold bearing mineralizing system of the Kis-Kuel Iron Oxide Copper-Gold deposit in Eastern Yakutia (Russia). Economic mineralization is localized within the apical zone of a granodiorite-diorite stock and represented by hematite, goethite, quartz, chalcopyrite, molybdenite, arsenopyrite, pyrite, native gold and bismuth (no signs of any ore mineralization were found outside the Kis-Kuel intrusive). The intrusive has a Late Cretaceous crystallization age (K–Ar) of 103 Ma. The Mo-bearing quartz vein yields a mineralization age (Ar–Ar) of 99.9±1.1 Ma and genetically relates to the granodiorite. Kis-Kuel breccia complex (KKBC) consists of a manto-type irregular shaped breccia body with arrays of variably mineralized veins and veinlets inside. The KKBC has a complete gradation from hematite-goethite altered granodiorites and more locally – diorites to intensely brecciated and hematite-goethite breccias. Multiple episodes of brecciating and veining with Fe-oxide-Cu-Au±Ag, porphyry Cu-Au±Bi, Ag-Pb and Mo+REE±Au mineralization occur in Kis-Kuel intrusive. In order to obtain more resources, the research Kis-Kuel target with IOCG mineralization was studied for molybdenum and rare earth minerals. Mainly, ore is quartz-bearing, Mo-Au-mineralized and strongly enriched in the rare earth elements (REE) material. The textures of REE minerals indicate crystallisation of monazite-(Ce) and xenotime as hydrothermal phases together with molybdenite and arsenopyrite. Analysis of quartz-molybdenite ore from the Kis-Kuel diorite-granodiorite intrusive shows previously unknown high concentrations of REE and Y, averaging 4.76 wt percent ∑REE + Y. Ore additionally contains 2.42 wt percent Mo, 8.8 g/t Au and 231 g/t Ag. We propose that one of the basic factors for mineralization styles at Kis-Kuel consists in the granitoids evolution and strongly differs from unevolved and mantle compatible compositions to highly evolved and fractionated intrusive rocks. The calc-alkaline evolution trend of the Kis-Kuel magmatic rocks is influenced by the accumulation of iron in ore. A significant part of the iron did not fractionated into high-iron melts, and separated into hydrothermal solutions with high grade gold concentrations. An extensively revised paragenetic model for Kis-Kuel deposit incorporates next four stages. Stage 1 dominated by widespread brecciating and iron metasomatism, which converted granodiorite rocks to Fe-oxide-Cu-Au ore. Stage 2 comprises chloritic and sericitic alteration and associated systems of linear quartz veins with Cu-Au-porphyry and Au-Bi mineralization. Stage 3 includes sericitic alteration and veining with quartz-molybdenite-native gold-REE minerals. Stage 4 consists of Ag-Pb veins.
1. Introduction
The Kis-Kuel IOCG deposit is located at the East Part of Russia, about 400 km north of Yakutsk and within the Verkhoyansk mobile belt of northeastern Yakutia. The fold-and-thrust belt forms part of a major orogenic system separating the Siberian North Asian Craton to the west from the immense expanse of accreted terranes that form most of Far East Russia [1, 2]. The Verkhoyansk belt extends for 2,000 km from the Laptev Sea to the Sea of Okhotsk. It is comprised of a greater than 7 km thick sequence of Late Precambrian to Triassic rocks deposited along the Palaeo-Pacific margin of the Siberian Craton, which developed due to rifting events during the Late Precambrian period and again during the Late Devonian to Early Mississippian periods [3]. Deformation during the Late Jurassic to Early Cretaceous occurred with low-grade metamorphism in the internal parts of the belt and in the emplacements of high-level granitic bodies [4].

Diamond and Precious Metal Geology Institute, Siberian Branch of the Russian Academy of Sciences discovered the Kis-Kuel deposit in 2008 and 2009. Fieldworks in 2018 led to the discovery of high Fe and Au grades in IOCG and Cu-Au porphyry style ores of the Kis-Kuel Breccia Complex (KKBC). After 2018 Kis-Kuel site was identified as an important Fe-Cu-Au with additional Ag, Pb, Bi and Mo deposit.

Magmatic contribution to the Kis-Kuel deposit is significant. Previous studies show that the Kis-Kuel magma process can be divided into four consecutive stages: diorite, granodiorite, granite and lamprophyre. Analyzes of diorite, granodiorite and rare-earth geochemical system of igneous rocks are characterized by behavior close to the CHARAC-system (26<Zr/Hf<46 и 24<Y/Ho<34) were the H/Ho – Zr/Hf ratios of the pair show a distribution close to chondrite (Zr/Hf = 36.6 and Y/Ho = 27.7). Minor deviations of the Kis-Kuel rocks from the CHARAC intervals indicate a lowly evolved magmatic system [5, 6].

Geochronological data of the Kis-Kuel intrusion based on K-Ar dating of rocks varies from 123 to 100 Ma [7]. Similar age also recorded for the crystallization of Western Verkhoyansk dike complexes (zircon): U-Pb SHRIMP-II, 102.9±1.4 and 104.9±1.4; the Endybal granitic pluton (zircon): U-Pb SHRIMP-II, 100.2±1.2 Ma [8]. The Ar-Ar method for dating light mica, associated with molybdenite (sample 6002), determined Kis-Kuel’s ore mineralization age as 99.9 ± 1.1 Ma.

Economic mineralization of KKBC is localized within the apical zone of a granodiorite-diorite stock and represented by hematite, goethite, quartz, rare chalcopyrite, arsenopyrite, pyrite, native gold and bismuth (no signs of any ore mineralization were found outside the Kis-Kuel intrusive). KKBC consists of a manto-type irregular shaped breccia body with arrays of variably mineralized veins and veinlets inside. The KKBC has a complete gradation from hematite-goethite altered granodiorites and more locally – diorites to intensely brecciated and hematite-goethite breccias. In order to obtain more resources, the research Kis-Kuel target with IOCG mineralization was studied for molybdenum and rare earth minerals. Mainly it is quartz-bearing, Mo-Au-mineralized and strongly enriched in the rare earth elements (REE) material. The textures of REE minerals indicate crystallisation of monazite-(Ce) and xenotime as hydrothermal phases together with molybdenite and arsenopyrite.

2. Materials and methods
All chemical analyses of intrusive rocks and ore minerals were carried out at the Diamond and Precious Metal Geology Institute, Siberian Branch, Russian Academy of Sciences (DPMGI SB RAS). Ore minerals were identified with scanning electron microscope JSM-6480LV with energy spectrometer INCA-Energy, with 20 kV of accelerating voltage at the cathode. Samples were prepared from polished sections with a sprayed thin conductive layer of carbon. Minerals in strongly oxidized ores were determined by x-ray phase analysis using D2 PHASER diffractometer. The Ar isotope composition was measured on a «Micromass-5400 Noble Gas» mass spectrometer at the Analytical
Center of the Institute of Geology and Mineralogy (Novosibirsk) in 2010. ICP analyses were performed in the laboratory of the Faculty of Geology and Survey of the North-Eastern Federal University in Yakutsk.

Figure 1. Geological map of the Kis-Kuel site, modified from Kostin [5] and the occurrences of the main ore styles showing discovered ore mineralization inside the Kis-Kuel intrusive. A red dot on the inset map shows the position of the Kis-Kuel ore cluster in the Verkhoyansk Range.

Sample preparation of the molybdenite-quartz ore included crushing and abrasion of the sample and subsequent analysis by ICP and atomic absorption methods. It turned out that almost all of the molybdenite was rolled into thin plates after attrition. Therefore, it was decided to dissolve the entire sample. A 10 g weighing sample was treated with a mixture of acids (HF + H₂SO₄, HNO₃) to wet salts, then to dissolved salts in hydrochloric acid and filtered into a 1000 dm³ flask. The filter with sediment was ashed, mixed with rafting (Na₂SO₃ + borax) and melted at a temperature of 910° C. The
alloy was dissolved in hydrochloric acid and transferred to a flask with the initial filtrate, brought to the mark with hot water. The analysis of rare earths and rare elements were carried out by atomic emission spectroscopy on an atomic emission spectrograph with an inductively coupled plasma iCAP 6300 AES ICP from Thermo Scientific Int. USA. To calibrate the device we used the following State Composition Standards: SSV-1, SGD-1, SGD-2, SG-1, ST-1, ST-2, SGHM-4, S1-3 and a line of multi-element (single-element) standard samples from Inorganic Ventures USA.

The determination of gold and silver in grab samples was done by atomic absorption spectroscopy on an atomic absorption spectrograph iCE 3500 from Thermo Scientific Int. USA. The standards used with ore samples analysis include GBM906-6 – GEOSTATS PTY LTD: Ag – 389.7 g/t and G908-8 – GEOSTATS PTY LTD: Au – 9.65 g/t.

3. Molybdenum-REE assemblage
Quartz, molybdenite, arsenopyrite, xenotime and monazite are the main minerals for this assemblage. Molybdenite occurrence within the Verkhoyansk mobile belt of northeastern Yakutia emphasize the consistent association with late Cretaceous plutonic granodioritic activity. It is a part of the porphyry gold-copper system which consists of disseminated copper minerals in rocks, veins and breccias, including quartz-molybdenite mineralization. The molybdenite-bearing mineralizing system of the Kis-Kuel is unusual in that it is quartz bearing, Mo-mineralized and strongly enriched in gold and bismuth bearing arsenopyrite [5] and the rare earth minerals. The textures of REE minerals indicate crystallization of monazite-(Ce) and xenotime as hydrothermal phases. Very small amounts of galena and sphalerite may be present in quartz veins with molybdenite. The basic mineral composition of molybdenite-REE assemblage was detected by X-ray phase analysis (figure 2). Quartz-molybdenitemonazite-xenotime veins at Kis-Kuel consistently crosscut granodiorite and occur as bands within the quartz-sericite veins (figure 3) were molybdenite forms euhedral platelets overgrowing the quartz.

![Figure 2](image_url)

**Figure 2.** A mixture of quarts, scorodite, molybdenite, muscovite, xenotime, arsenopyrite, monazite and betpakdalite was determined by x-ray phase analysis using D2 PHASER diffractometer (sample 88100).
Molybdenite is of economic value at Kis-Kuel, and mainly occurs in mineralized zones of hydrothermal alteration with quartz, muscovite and sericite. The ore is partially oxidized, and contains scorodite and betpakdalite. Most common is lamellar molybdenite in quartz. It also occurs as 0.1 to 1 cm flakes disseminated in quartz-mica veins, or as fine-grained films filling the fissures. Arsenopyrite is a typical primary sulfide mineral in Kis-Kuel molybdenum ore. Arsenopyrite forms crystals and aggregates up to 1-5 cm in quartz and includes native gold, bismuth, bismite and neyite. Native bismuth contains a small amount of silver and gold. The admixture of gold and rare tellurium are also presents in neyite [5]. We assume that monazite and xenotime belongs to hydrothermal phases within the Kis-Kuel deposit. REE enrichment in hydrothermal system is ascribed to magmatic process that can concentrate REE through liquid immiscibility or in primary REE-rich minerals such as phosphates (monazite and xenotime) crystallizing from magma. Monazite and xenotime usually occurs in small euhedral isolated crystals or as intergrown aggregates with arsenopyrite and molybdenite. The REE mineral assemblage of the Kis-Kuel system illustrated in the figure 4.

Figure 3. Mo-REE mineral assemblages of the Kis-Kuel Cu-Au-porphyry complex. A – Quartz-molybdenite-monazite-xenotime mineralisation in Cu-Au-porphyry complex. Sample 88100: Au – 8.8 g/t, Ag – 231 g/t, Mo – 2.42%, ΣREE + Y – 4.76%. B – Quartz-sericite mineralization associated with molybdenite and REE-mineralisation. This sample with light mica has been used for Ar-Ar dating.

Figure 4. A backscattered electron images of molybdenite and REE mineralization (sample 88100). A - Lamellar molybdenite in quartz; B - Quartz-arsenopyrite-monazite-xenotime paragenesis; B - Slice of a prismatic xenotime crystal - characteristic tetragonal syngony; D - A slice of a monazite crystal is represented by a rhombic prism, typical for monoclinic syngony; D and E - Varieties of intergrowths of monazite and xenotime (abbreviations: Mo - molybdenite, Qz - quartz, Apy - arsenopyrite, Xtm - xenotime, Mnz - monazite).
Gold and copper mineralization consists of disseminated copper minerals in rocks, veins and breccias and is associated with quartz-molybdenite mineralization. Permafrost processes destroy the surface of mineralized granodiorite intrusive (figure 5A). In porphyry environment, wall-rock alteration is linked to narrow veins, commonly 0.1 to 5 cm in width that typically makes up less than 1-5 volume percent of ore (Figure 5B). Intrusion-related copper-gold mineralization with a low sulphide mineral content (mostly <5 vol%), typically comprises arsenopyrite, chalcopyrite, pyrite and lacks magnetite or hematite. High-grade copper-gold ore with iron and copper minerals is strongly oxidized (Figure 5C). X-ray phase analysis on D2 PHASER diffractometer identified an arthurite CuFe$_2$((H$_2$O)$_4$(OH)$_2$(AsO$_4$)$_2$), jarosite (K$_{0.95}$(H$_3$O)$_{0.05}$Fe$_3$(SO$_4$)$_2$(OH)$_6$) and scorodite FeAsO$_4$(H$_2$O)$_2$. Native gold presents in both arthurite and jarosite (figure 5D).

Figure 5. The Cu-Au-porphyry mineral assemblages inside Kis-Kuel Breccia Complex. A – Outcrop of an array of ferrous-quartz multi-directional veinlets with Cu-Au-porphyry mineralization in the apex of the Kis-Kuel granodiorites. The surface of the intrusion is strongly damaged by permafrost processes, ore is partially oxidized. B – Quartz + Fe-oxide + arsenopyrite veinlets cutting granodiorite: Cu – 0.17-0.24%, Ag – 20-196 g/t, Au – 0.38-4.6 g/t. Alteration is limited to thin selvages adjacent to the veinlets. C - Quartz-arthurite-jarosite fragments from Cu-Au-porphyry ore in granodiorites: FeOtot – 33.42%, Cu – 3.57%, Ag – 329 g/t, Au – 64.48 g/t. D – Native gold inclusion in arthurite and jarosite.

4. Results and discussions

Analysis of quartz-molybdenite ore from the Kis-Kuel diorite-granodiorite intrusive shows previously unknown high concentrations of REE and Y, averaging 4.76 wt percent of $\Sigma$REE + Y. Additionally ore contains 2.42 wt percent Mo, 8.8 g/t Au and 231 g/t Ag (table 1). Other elements in quartz-molybdenite-REE ore (in %): As-6.56, Co-0.045, Cr-0.036, Cu-0.12, Ga-0.0026, Hf-0.0029, Nb-0.0073, Ni-0.0047, Pb-0.94, Rb-0.0029, Sn-0.0084, Sr-0.0217, Ta-0.0093, Th-0.0294, V-0.0028, Zn-0.11, Zr-0.0203.
Table 1. Molybdenite-REE ore analysis and recoverable values of the products.

| Commodity | Oxide and metal content | Oxide and metal price | Production cost, USD/t |
|-----------|-------------------------|-----------------------|------------------------|
| Ce₂O₃     | 12.18                   | 2.35                  | 28.63                  |
| Dy₂O₃     | 3.40                    | 237                   | 806.52                 |
| Er₂O₃     | 2.09                    | 23                    | 47.99                  |
| Eu₂O₃     | 0.14                    | 31                    | 4.38                   |
| Gd₂O₃     | 2.27                    | 26.882                | 60.98                  |
| Ho₂O₃     | 0.67                    | 50.9                  | 33.90                  |
| La₂O₃     | 6.48                    | 3.5                   | 22.68                  |
| Lu₂O₃     | 0.22                    | 587                   | 130.65                 |
| Nd₂O₃     | 8.25                    | 43.011                | 355.03                 |
| Pr₂O₃     | 0.00                    | 48.5                  | 0.00                   |
| Sm₂O₃     | 2.59                    | 1.75                  | 4.52                   |
| Sc₂O₃     | 0.03                    | 934                   | 31.89                  |
| Tb₂O₃     | 0.53                    | 519                   | 275.17                 |
| Tm₂O₃     | 0.23                    | 20000                 | 4569.39                |
| Y₂O₃      | 15.93                   | 3                     | 47.78                  |
| Yb₂O₃     | 1.73                    | 14.6                  | 25.29                  |
| Mo        | 24.25                   | 29.45                 | 714.15                 |

| Commodity | Oxide and metal content | Oxide and metal price | Production cost, USD/t |
|-----------|-------------------------|-----------------------|------------------------|
| Au        | 8.8                     | 47.99                 | 422.35                 |
| Ag        | 231                     | 0.57                  | 132.72                 |

Total Production cost, USD **7714.05**

Metal prices effective from October 20, 2019. Rare earth metals prices obtained from Asian Metal market at http://www.asianmetal.com, molybdenum - from http://www.generalmoly.com, gold and silver – from https://www.metaltorg.ru.

Xenotime developed as both individual prismatic crystals and hosted in quartz and monazite. Xenotime varies in size and is not zoned. Microprobe analysis of xenotime showed significant admixture of Sm, Gd, Tb, Dy, Ho, Er and Yb (table 2). Kis-Kuel monazite contains different rare earth metals and represents a group of monazite-(Ce) with the Ce, La, Nd – dominant members of the group (Table 3).

Table 2. Representative microprobe analysis of xenotime (sample 88100), wt. %.

| P₂O₅ | Sm₂O₃ | Gd₂O₃ | Tb₂O₃ | Dy₂O₃ | Ho₂O₃ | Er₂O₃ | Yb₂O₃ | Y₂O₃ | Total |
|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 33.77 | 1.07  | 6.22  | 2.54  | 8.84  | -     | 4.34  | 4.19  | 38.72 | 99.69 |
| 30.24 | 4.35  | 5.55  | 0.85  | 9.01  | -     | 3.04  | 5.49  | 38.26 | 96.79 |
| 29.87 | 8.48  | 3.4   | 4.09  | 8.01  | -     | 2.83  | 6.15  | 38.75 | 99.58 |
| 31.25 | 1.43  | 9.13  | 2.23  | 11.96 | -     | 4.33  | 2.42  | 35.7  | 98.45 |
| 31.9  | 2.93  | 5.88  | 1.3   | 1.06  | 3.33  | 4.34  | 35.68 | 97.42 |
| 31.28 | 1.51  | 5.77  | 1.93  | 13.32 | 3.74  | 4.17  | 2.32  | 36.78 | 100.82 |
| 31.58 | 0.25  | 8.93  | 3.24  | 11.92 | 0.42  | 3.75  | 3.27  | 33.09 | 96.45 |
| 34.71 | 1.77  | 3.51  | 1.92  | 5.8   | -     | 4.55  | 46.85 | 99.11 |
| 29.76 | 7.41  | 2.82  | -     | 6.66  | 2.19  | 4.47  | 5     | 40.17 | 98.48 |

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Table 3. Representative microprobe analysis (wt. %) and calculated mole fraction of yttrium and temperatures for monazites in sample 88100.

| La2O3 | Ce2O3 | Pr2O3 | Nd2O3 | Sm2O3 | Gd2O3 | Y2O3 | P2O5 | Total  | X_{Ymz} | T°C  |
|-------|-------|-------|-------|-------|-------|-------|-------|--------|---------|------|
| 12.04 | 29.71 | 5.12  | 18.21 | 3.77  | 2.19  | 0.65  | 28.59 | 100.28 | 0.0255  | 174  |
| 11.78 | 29.08 | 4.98  | 16.89 | 4.36  | 4.81  | 0.64  | 28.15 | 100.69 | 0.0251  | 167  |
| 13.07 | 28.13 | 5.88  | 16.83 | 3.78  | 3.03  | 0.97  | 26.04 | 97.73  | 0.0379  | 350  |
| 15.08 | 34.92 | 4.26  | 16.23 | 2.59  | 3.18  | 0.84  | 25.62 | 102.72 | 0.0329  | 287  |
| 17.53 | 30.64 | 6.98  | 12.96 | 2.02  | 3.08  | 1.03  | 27.03 | 101.27 | 0.0403  | 376  |
| 13.38 | 31.12 | 3.92  | 19.68 | 3.68  | 3.56  | 0.79  | 27.62 | 103.75 | 0.0309  | 260  |
| 15.14 | 32.32 | 2.27  | 12.88 | 1.15  | 1.69  | 1.02  | 26.21 | 92.68  | 0.0399  | 372  |

R. Gratz, W. Heinrich [9, 10] calibrated the partitioning of yttrium as a geothermometer through experiments on the CePO$_4$–YPO$_4$ binary, as:

$$T = \ln \frac{100 X_{Ymz}}{1.459 + 0.00852 P} \times 2.2745 \times 10^{-3}$$

where T is the equilibrium temperature in °C, X_{Ymz} is the mole fraction of yttrium in monazite, and P is pressure in kbar. K. Viskupic and K.V. Hodges showed that pressure changes have little effect on temperature [12]. We used data from W. Heinrich et al. [11] who found that monazite-xenotime pair is stable at 3 kbar pressure in ours calculation using Eq. (1).

5. Conclusions

The presence of molybdenum and rare earth mineralization together with Cu-Au-porphyry mineral assemblages inside Kis-Kuel Breccia Complex provides a good opportunity for more resource potential of Kis-Kuel IOCG deposit. Occurrence of high REE and Y concentrations in the Kis-Kuel ore breccia together with previously documented hematite, gold and copper [5, 6] suggest that mineralization belongs to iron oxide-copper-gold (IOCG) deposit style. Other Mo mineralization of Mesozoic age in the East Yakutia and elsewhere in the world may have potential for REE and Y resources. IOCG deposits with abundant molybdenum should also be evaluated for possible undiscovered light and heavy REE and yttrium mineralization.

Our study has demonstrated that hydrothermal monazite and xenotime can form large clusters. Scanning electron microscopy indicated REE and Y impurity in monazite and xenotime that form either euhedral to subhedral crystals complex intergrowths with quartz, arsenopyrite, molybdenite and native gold suggesting coeval As, Au and REE + Y mineralization during the Mesozoic. Kis-Kuel monazite does not contain impurities of Th, U, and Si at all and is not zonal like many varieties of this mineral of magmatic and pegmatite origin [13]. This might mean that the formation of monazite occurred in one hydrothermal stage.

Using the partitioning of the yttrium between coexisting monazite and xenotime allowed us to establish the temperature range for the formation of xenotym-monazite paragenesis in the range from 376 to 167 °C. The obtained data (see table 3) indicates a limited solid solution between the rare-earth phosphates monazite and xenotime and characterizes low temperature for molybdenite-REE mineral formation.

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