Mineralization in the andesitic lava from Kildyam volcanic complex, central Yakutia, Russia

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Abstract. This contribution presents the first detailed analysis of a new volcanic succession of olivine-pyroxenites, andesite, and dacite discovered in the Kildyam Late Jurassic complex in Central Yakutia. Petrographic and microprobe studies confirmed the liquid immiscibility in silicate melts during crystallization. Immiscible liquids are preserved as globules of one glass in another in andesites and as melted inclusions of native iron in matrix, clinopyroxene and plagioclase phenocrysts. Our analyses reveal the complex textural relationships between silicates and Fe-oxides, native iron and (Cu, Pb, Ag and Au)-rich phases, and provide unequivocal textural evidences, not observed previously. Purpose of this research is to preserve a very important data on IO (Iron Oxide) or IOCG (Iron Oxide Copper Gold) mineralization. Obtained results support occurrence and diverse of gold, silver, copper and lead minerals in magnetite lavas. During the early stage of fine-grained subvolcanic olivine-clinopyroxenite end pyrrhotite, globular igneous sulfides is a first proposed style of economic deposit formation. The second proposed style of economic mineralization in Kildyam is to be a magnetite-bearing lava; iron enrichment of the melilitic melt phase, followed by iron depletion and silica enrichment. The vesicle-hosted alloys and sulfides provide significant new data on metal transport and precipitation from high-temperature magmatic vapors. During syneruptive vapor phase exsolution, volatile metals (Cu-Zn, Fe-Al-Cu, Ni-Fe-Cu-Sn) and Ag-Cu-sulfides contribute to the formation of economic concentrations. Major conclusions contribute to 3-step genetic model. (1) Early-formed magmatic minerals led to partial dissolution of olivine-clinopyroxenite and their enrichment in Cu, Co and Ni relative to other metals, while troilite globules droplets grew. (2) First stage of division into two immiscible silicate and sulfide melt liquids (a) K-rich dacitic and rhyolitic glass, and (b) vesicles of heavy sulfide minerals with a large segregations and drops of native iron. (3) Lava of fused magnetite crystals and voids enriched in silver and gold, and (b) globular disseminated chalcopyrite in mineralized melilitic rocks.

1. Introduction
Recent discovery of magnetite lavas, associated assemblages of sulfides (troilite, pyrrhotite, chalcopyrite and pyrite) and metals (iron, copper, gold, and silver) from Late Jurassic volcanic succession in Central Yakutia, modifying the Kildym metal budget and distribution. Evidence of coexisting iron + precious metal + brine assemblages exists where native metals accompanied by halite. Occurrence of diverse iron, copper and silver mineral associations documented in (a) lava of fused magnetite crystals and voids; (b) globular disseminated chalcopyrite in mineralized melilitic rocks (c) complex shaped and sized globules hosted of chalcopyrite-troilite intergrowths in olivine-
clinopyroxenite and; (d) large segregations and drops of native iron; (e) vesicles filled with heavy sulfide minerals [1].

All Kildyam volcanic processes occur in connection with the iron enrichment. Low sulfur content in the Kildyam magma come initially from fayalite, clinopyroxene, plagioclase and magnetite parent magma (samples 1039 and 1051 SiO₂ - 41.17-37.44, TiO₂ - 0.88-0.81, Al₂O₃ – 9.31-11.76, Fe₂O₃ – 15.02-7.35, FeO – 16.3-26.78, MnO – 1.51-2.21, MgO – 1.63-1.19, CaO – 12.03-9.56, Na₂O – 0.21-0.26, K₂O – 0.11-0.12, P₂O₅ – 0.07-0, H₂O²⁻ - 0.67-0.73, H₂O⁰⁻ - 0.54-0.5, CO₂ – 0-0.07, S – 0.47-0.75, LOI – 0.69-0.91).

(A) During the early stage of fine-grained subvolcanic olivine-clinopyroxenite end pyrrhotite; globular igneous sulfides is a first proposed style of economic deposit formation.

(B) The second proposed style of economic mineralization in Kildyam is to be a magnetite-bearing lava; iron enrichment of the melilitic melt phase, followed by iron depletion and silica enrichment.

(C) The vesicle-hosted alloys and sulfides provide significant new data on metal transport and precipitation from high-temperature magmatic vapors. During syneruptive vapor phase exsolution, volatile metals (Cu-Zn, Fe-Al-Cu, Ni-Fe-Cu-Sn) and Ag-Cu-sulfides contribute to the formation of economic concentrations.

Kildyam magnetite crystallization mark the end of absolute iron enrichment in magma, the same way as in the Skaergaard intrusive [2], El Laco volcano [3,4], El Romeral diodite [5]. On the other hand, melilitic and silica-rich liquids balances the composition corresponding to andesite. Accumulation of large sulfide volumes, fayalite and augite near the surface, indicate possible existence of substantially heavier rocks located deeper. This is confirmed with a presence of an unusual complicated mineral phase of spinelide, discovered in andesite-variolitic lavas; it is a mix of ulvespinel (Fe₂TiO₄) ± spinel (MgAl₂O₄), enriched with Nb. Back-scattered electron image show fragments of ulvospinele skeletal crystal in glass matrix, which most likely came from olivine-clinopyroxenite.

Our research confirmed that tholeiitic trend of iron-rich olivine-pyroxenites evolves towards two immiscible liquids - magnetite lava and melilitite matrix. Further evolution lead to the separation of native iron and the transition of lavas to the silica-rich calc-alkaline trend. Petrographic and microprobe studies confirmed the liquid immiscibility in silicate melts during crystallization. Immiscible liquids are preserved as globules of one glass in another in andesites and as melted inclusions of native iron in matrix, clinopyroxene and plagioclase phenocrysts.

2. Mineralization
Tholeiitic trend of Kildyam iron-rich olivine-pyroxenites evolves towards two immiscible liquids - magnetite lava and melilitite matrix. Variolitic lavas of Kildyam mineral assemblage with native iron, include different amount of magnetite, troilite, pyrrhotite and pyrite, and considered common in the tholeiite trap formation of the Siberian platform. Native iron occurs as large segregations and drops in the rock-forming andesites and in the phenocrysts of plagioclase and pyroxene. Impurities of Co – 0.04-2.89%; Ni – 0.01-1.09% installed in native iron.

Mineralized vesicles in lava are usually grouped in chains connected with cracks. Most of them are hollow and only some of them filled with cristobalite, metallic sublimates, sulphides and iron oxides. The metallic sublimates in the vesicle walls of mafic volcanic lava are morphologically and compositionally similar among the volcanoes. Based on microprobe analyses, the major of ore bearing vesicles content in Kildyam Volcanic Complex are Cu-Zn, Al-Fe-Cu and Fe-Ni-Cu-Sn alloys, Ag, Zn,
Pb, Fe and Cu, Ag sulfides. Among diagnosed sulphides are Ag-tetrahedrite, argentite, galena, sphalerite, chalcopyrite, pyrite, troilite. Most common mineral in volcanic vesicles is cristobalite.

2.1 Troilite globules in olivine-clinopyroxenite
According to Craig and Kullerud [6] troilite, pirrhotite, chalcopyrite, and ± pentlandite is a tipical sulfide assemblage from mafic magmas. Segregations of subspherical agglomerations interpreted as sulfide liquids; in places form elongated clusters up to 3 cm in length (Figure 1A). Globules as sulfide phases in Kildyam olivine-clinopyroxenite melt (about 89-mol % of Fa) completely filled with sulfides and consisting mainly of pyrrhotite and less often troilite. Subvolcanic level contains subordinate amounts of cracks at all; silver sulfides and gold rare. Higher up there are more cracks and voids, and the mineralization increases. Sulfide liquids enriched in Co, Ni and most valuable intergrowth are alloys Au,Ag,Cu,Fe (Figure 1B, sample 1039-1/8(1-7)) and sulfides of Ag(Fe)2S (Figure 1C, sample 1039-1/32(2-3) and Figure 1D, 1039/8(1-2)).

Figure 1. Mineralization in olivine-clinopyroxenite, with sulfides (troilite and pyrrhotite) forming globules and tubes [(A) close-up photograph; (B-D) back-scattered electron images)]. A – Polished olivine-clinopyroxenite sample with immiscible sulphide segregations of elongated tube morphology; close up to the foaming begin (sample 1039-1). B – Vesicles and degassing chanels partially filled with gold; their fineness (650–1000‰) (sample 1039-1/8(1-7)). C – Vesicles and degassing chanels partially filled with argentite grains (sample 1039-8/32(1-8)). D – Argentite performs a void in a degassing chanel (sample 1039/8(1-2)).

2.2 K-rich dacitic and rhyolitic glass, and vesicles of heavy sulfide minerals
Vesicle textures in volcanic rocks save data on the history of magmas [7]. In products from effusive and explosive andesitic and basaltic eruptions, vesicles have been used to investigate the emplacement of lava flows from vents, and mineralisation. Examples of world-class eruptive activity are Strombolian eruptions [8]; Mount Etna, Italy [9]; magma rise and fragmentation in Hawaiian-style fire fountains [10]. Due to the speed of bubble formation, rising assemblage of porous balls (Figure 2A), pyrite and
bartonite (Figure 2B and C) in dacitic and rhyolitic lava occur foaming and rapid solidification. In many cases, these globules partially fill subspherical intercumulus spaces within vesicle with sulfides. Sulfide-silicate liquid immiscibility lead to accumulation of heavy sulfide minerals in voids. Hosting K-rich dacitic glass (sample 1044-7/9(6) show the bulk of SiO$_2$ – 70.19, Al$_2$O$_3$ – 9.48, FeO$_{tot}$ – 9.73, MnO – 0.43, CaO – 1.77, K$_2$O – 6.49, Total – 98.08), and K-rich rhyolitic glass (sample 1044-7/8(4) show the bulk of SiO$_2$ – 75.05, Al$_2$O$_3$ – 11.31, FeO$_{tot}$ – 2.77, CaO – 1.45, K$_2$O – 7.83, total 99.05).

2.3 Large segregations and drops of native iron
Native iron occurs as large segregations and drops in the rock-forming andesites (Figure 3A and B); typically, iron droplets are found in large pyrrhotite splices, where 1 to 5 droplets can be present together. Many drops of native iron located in sanidine (Figure 3C) directly indicate mineral pair as immiscible liquid. Immiscible texture developed in glass and hedenbergite microlites; plagioclase (labrador) is free of liquid iron micro-spherules (Figure 3D). Most common are drops of native iron in pyrrhotite and spherical separation of pyrrhotite with fused drops of native iron inside; impurities of Co – 0.04-2.89%; Ni – 0.01-1.09% are commonly installed in native iron.

![Figure 2. Back-scattered electron images support a diverse style and shape of bubble foaming. A - Sulfide-silicate liquid immiscibility leads to accumulation of heavy sulfide minerals (sample 1030-8/37) in rhyolitic glass. B - The inner walls of large bubbles filled with Bartonite, outer - with pyrite; fine grains are also of Bartonite and pyrite (sample 1030-8/27). C - The internal parts and fasteners of the bubbles filled with Bartonite. Intergrowth of Cu-alloy and Bartonite (sample 1044-7/35 show the bulk of Bartonite S – 39.89, K – 8.82, Fe – 50.47, Total – 99.18). Abbreviations: Brt – Bartonite, Cu – Copper native, Hem – Hematite, Pi – Pyrite, Po – Pyrrhotite.](image-url)
Figure 3. Large segregations and drops of native iron. A - A drop of native iron in pyrrhotite (sample 1030-4/3(1)). B - Spherical separation of pyrrhotite with fused drops of native iron inside, in glass matrix (sample 1030-1/23(1)). C – Immiscible texture developed in sanidine and liquid iron micro-spherules (sample 1030-1/30(1-3)). D - Immiscible texture developed in glass and hedenbergite microlites; plagioclase is free of liquid iron micro-spherules (sample 1030-8/23(40)). Abbreviations: GLS – Glass matrix; Hd – Hedenbergite; liq Fe – Native iron; Po – Pyrrhotite; Wol – wollastonite.

2.4 Lava of fused magnetite crystals and voids
Magnetite lava flows known in the Pleito-Melon District of the Chilean iron belt, El Laco volcano, traps of the Siberian platform. Magnetite is widespread at the Kildyam volcano; in solid ores, magnetite observed in the form of small fused grains and voids. In different sections of lava flows, increased content of MgO, MnO and TiO₂ refers to the peculiarity of the composition of magnetite. Fe-rich mineralization generally hosted by two generation of zoned magnetite gains with raw alloys and sulfides (Figure 4A). Most valuable intergrowth with metals and sulfides found in voids. Alloys: pure Au (Figure 4B, sample 1064-4/7(1-8)); Cu-Sn-Fe-Ni alloy [sample 1064-1/9(1-8) and 1064-1/15(1-7)]; FeCoNiCu alloy [sample 1064-b/4(2-3)]; Cu-Fe-Co-Ni alloy [sample 1064-b/4(1) and 1064-b/6(1-7)]. Sulfides: (Cu,Fe,Ag)₃(Sb,As)S₄ (Figure 4C, sample 1064-2/5(1-5)); Ag₃S (Figure 4D, sample 1064-1/14(1-7) and 1064-1/17(1-2)); CuFeS₂ [sample 1064-3/16(1-4)], and FeAsS₂ [sample 1064-b/17(1-7)].
Figure 4. Back-scattered electron images of magnetite lava and minerals in voids. A – About 60% of magnetite lava consist of small fused grains, and the rest 40% are voids (sample 1064-1/8). B–D – Typical void morphology for the degassing channels with some of significant alloys and sulfide sublimates; voids connected with degassing channels, and grouped into extended chains. B – A plate of pure gold closing degassing channel (sample 1064-4/7). C – Tetrahedrite cristal attached to void wall, sample 1064-2/5 [1]. D – Crystal sprout of Cu and Fe argentit in a degassing chanel (sample 1064-1/3). Abreviations: Ag – Argentit, Au – Gold native, Mt – Magnetite, Tr – Tetrahedrite.

2.5 Globular disseminated chalcopyrite in mineralized melilitic rocks
Melilitic rocks (Figure 5A) contains sulfides in subordinate amounts. This chalcopyrite interpreted to have formed predominantly by accumulation of immiscible sulfide droplets, and is believed to preserve a very important data on IO (Iron Oxide) or IOCG (Iron Oxide Copper Gold) mineralization. Being in the common ore style, and physically separates from Fe-rich minerals, Si-rich conjugate ground mass host chalcopyrite globules inside barite (Figure 5B).

Figure 5. Back-scattered electron images of melilitic rock. A – Mellite intergrowth (prevailing), and barite; about 3% of voids (sample 1064-3/12). B – Mellite with some magnetite, pyroxene, pyrrhotite and celsian; chalcopyrite from liquid droplets (sample 1064-3/18). Abreviations: Ba – barite, Cls – celsian, Ccp – chalcopyrite, Mll – melilite, Mt1 – Ti-magnetite, Po – Pyrrhotite, Px1 – Fe– pyroxene, Px2 – low-Fe pyroxene.
3. Results and discussions
Volcanic breccia and iron-oxide mineralization from the Kildym succession contain (a) oxides: hematite, magnetite, Ti-magnetite; phenocrysts (sample 1030-1/20) of ilmenite, rutile, pseudorutile, and ilmenorutile (Ti,Nb,Fe+++O₂); sulfides: argentite, chalcopyrite, bartonite, pyrite, pyrrhotite, tetrahedrite, troilite; alloys: Au, Au-Ag-Cu-Fe, Cu, Cu-Zn, Fe-Al-Cu, Ni-Fe-Cu-Sn. (Table 1, 2)

Table 1. Gold and gold-bearing galena in Kildym lavas

| Sample     | Au  | Ag  | Pb  | Cu  | Fe  | S   | Total |
|------------|-----|-----|-----|-----|-----|-----|-------|
|            |     |     |     |     |     |     |       |
|            |     |     |     |     |     |     |       |
| In troilite globules in olivine-clinopyroxenite |     |     |     |     |     |     |       |
| 1039-1/7(1)| 64.11 | 9.31 | -   | 14.86 | 10.39 | -   | 98.66 |
| 1039-1/8(1)| 62.21 | 11.17 | -   | 16.41 | 8.00  | -   | 97.79 |
| 1039-1/8(2)| 62.72 | 10.40 | -   | 16.40 | 9.46  | -   | 98.99 |
| 1039-1/8(3)| 62.79 | 10.04 | -   | 16.83 | 8.64  | -   | 98.30 |
| 1039-1/8(5)| 62.05 | 10.57 | -   | 16.57 | 10.56 | -   | 99.74 |
| 1039-1/8(6)| 62.73 | 10.74 | -   | 16.72 | 7.19  | -   | 97.37 |
| 1039-1/8(7)| 63.63 | 10.54 | -   | 15.03 | 8.15  | -   | 97.36 |

|            |     |     |     |     |     |     |       |
| In lava of fused magnetite crystals and voids |     |     |     |     |     |     |       |
| 1064-4/7(1)| 99.83 | -   | -   | -   | -   | -   | 99.83 |
| 1064-4/7(2)| 99.97 | -   | -   | -   | -   | -   | 99.97 |
| 1064-4/7(3)| 99.59 | -   | -   | -   | -   | -   | 99.59 |
| 1064-4/7(4)| 99.42 | -   | -   | -   | -   | -   | 99.42 |
| 1064-4/7(5)| 95.64 | 3.55 | -   | -   | -   | -   | 99.19 |
| 1064-4/7(6)| 100.82 | - | -   | -   | - | - | 100.82 |
| 1064-4/7(7)| 96.43 | -   | -   | -   | 1.63 | -   | 98.06 |
| 1064-4/7(8)| 99.92 | -   | -   | -   | -   | -   | 99.92 |
| 1044-2/2(1)| 1.31 | -   | 82.56 | 0.86 | - | 14.29 | 99.82 |
| 1064-2/2(2)| 1.69 | -   | 83.98 | 0.13 | - | 14.25 | 100.06 |

*Earlier (Kostin, 2021) Fe, Cu alloys and sulfides were.*

Table 2. Argentite and silver-bearing tetrahedrite in Kildym lavas

| Sample     | Zn  | Fe   | Cu   | Ag  | Sb  | As  | S   | Total |
|------------|-----|------|------|-----|-----|-----|-----|-------|
|            |     |      |      |     |     |     |     |       |
|            |     |      |      |     |     |     |     |       |
| In troilite globules in olivine-clinopyroxenite |     |     |     |     |     |     |     |       |
| 1039-1/32(2)| - | 1.73 | -   | 85.60 | -   | -   | 12.37 | 99.71 |
| 1039-1/32(3)| - | 1.34 | -   | 85.16 | -   | -   | 12.62 | 99.12 |

|            |     |      |      |     |     |     |     |       |
| In lava of fused magnetite crystals and voids (2.4) |     |     |     |     |     |     |     |       |
| 1064-1/14(1)| - | 0.76 | 0.39 | 82.91 | -   | -   | 15.83 | 99.89 |
| 1064-1/14(2)| - | 1.25 | 1.07 | 82.89 | -   | -   | 13.64 | 98.84 |
| 1064-1/14(3)| - | 1.75 | 1.16 | 80.78 | -   | -   | 15.25 | 98.95 |
| 1064-1/14(4)| - | 2.00 | 0.46 | 82.01 | -   | -   | 13.49 | 97.96 |
| 1064-1/14(5)| - | 0.80 | 0.87 | 82.61 | -   | -   | 14.78 | 98.08 |
| 1064-1/14(6)| - | 1.39 | 1.43 | 81.60 | -   | -   | 13.62 | 98.03 |
| 1064-1/14(7)| - | 0.66 | 0.06 | 81.91 | -   | -   | 15.35 | 97.98 |
| 1064-2/5(1)| 4.22 | 2.61 | 34.27 | 6.27 | 24.16 | 2.21 | 23.55 | 100.25 |
| 1064-2/5(2)| 5.38 | 2.87 | 32.98 | 7.68 | 22.32 | 1.71 | 25.40 | 98.32 |
| 1064-2/5(3)| 4.11 | 2.86 | 33.15 | 6.23 | 25.56 | 2.62 | 24.12 | 98.66 |
| 1064-2/5(4)| 5.22 | 2.63 | 34.88 | 6.71 | 22.69 | 1.37 | 24.89 | 98.39 |
| 1064-2/5(5)| 4.61 | 2.55 | 35.16 | 6.06 | 22.93 | 2.25 | 25.34 | 97.88 |
The Kildyam occur as massive, sub horizontal tabular bodies, crosscutting fider dikes, and as stratified, fragmental material lava flows. Major conclusions contribute to 3-step genetic model. (1) Early-formed magmatic minerals led to partial dissolution of olivine-clinopyroxenite and their enrichment in Cu, Co and Ni relative to other metals, when troilite globules droplets grew. (2) First stage of division into two immiscible silicate and sulfide melt liquids; (a) K-rich dacitic and rhyolitic glass, and (b) vesicles of heavy sulfide minerals with a large segregations and drops of native iron. (3) Lava of fused magnetite crystals and voids enriched in silver and gold, and (b) globular disseminated chalcopyrite in mineralized melilitic rocks (Figure 6).

Figure 6. Model for the liquid immiscibility in Kildyam lavas

4. Conclusions
We believe the final magnetite ore bodies formed from iron oxide magma that intruded the local volcanic sequence and in places erupted at the surface. Occurrence of diverse gold, silver, copper and lead minerals in magnetite-lavas ore preserve a very important data on IO (Iron Oxide) or IOCG (Iron Oxide Copper Gold) mineralization [11]. Iron native and as sulfides with copper, enriched from the liquid sulfide droplets; copper, led, silver and gold precipitated from high-temperature late magmatic fluids [12–14].

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