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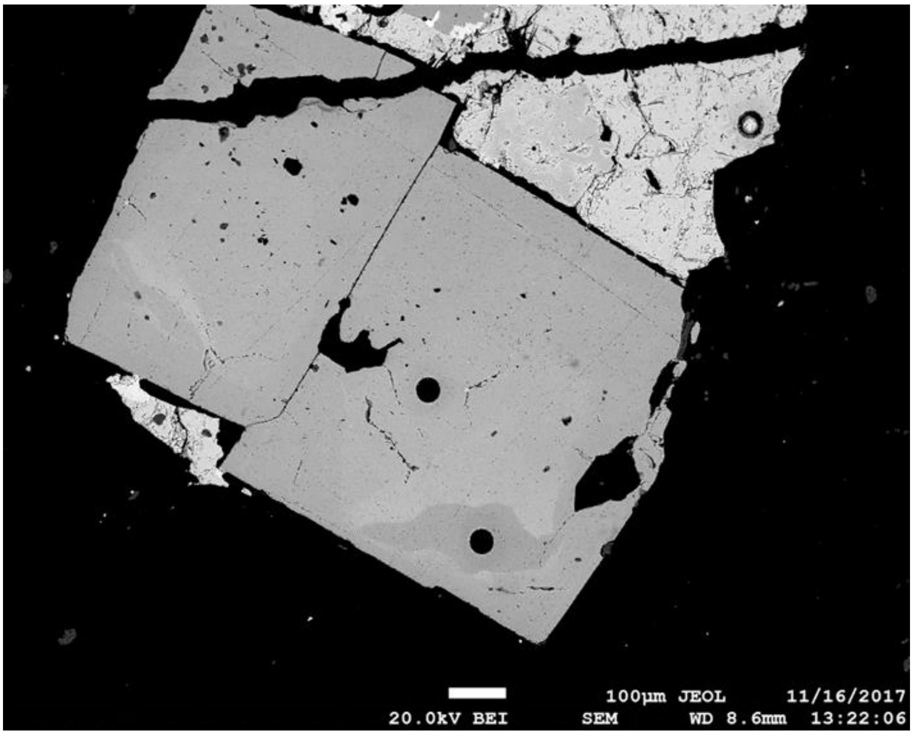

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Cover Figure:

SEM-BSE image of euhedral pyrite in contact with chalcopyrite from the Juomasuo Au-Co deposit; visible are laser ablation pits from in situ sulfur isotope analytical work via LA-ICP-MS.

MIKAEL VASILOPOULOS

Sulfide trace elements, isotope geochemistry and lithogeochemical characteristics of orogenic gold deposits with typical and atypical metal associations from northern Finland

Academic dissertation to be presented with the assent of the Doctoral Training Committee of Technology and Natural Sciences of the University of Oulu for public defence in Auditorium L5, Linnanmaa, on the 25th of August 2023, at 12:00 p.m.

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Sulfide trace elements, isotope geochemistry and lithogeochemical characteristics of orogenic gold deposits with typical and atypical metal associations from northern Finland

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ABSTRACT

The Paleoproterozoic Central Lapland and Kuusamo belts of northern Finland host several examples of orogenic gold mineralization as is common for Precambrian greenstone belts in Finland and globally. Approximately half of known occurrences of orogenic gold in the Central Lapland belt and most of the occurrences in the Kuusamo belt are characterized by significant enrichment of base metals in addition to Au and have been classified as orogenic gold deposits with an atypical metal association. Despite a long exploration and research history in these two greenstone belts there are still open questions regarding the processes that led to the formation of both Au-only and atypical orogenic gold deposits. The aim of this study is to combine several geochemical methods together with mineralogical observations with the purpose of investigating the evolution of hydrothermal processes that led to the formation of orogenic gold deposits in northern Finland. This dissertation comprises three research articles, and three orogenic gold deposits with different metal associations were chosen as research targets: the Juomasuo Au-Co deposit from the Kuusamo belt, and the Hirvilavanmaa Au-only and Naakenavaara Cu-Co-Ni-Au deposits from the Central Lapland belt. This study presents sulfide trace element and sulfur isotope data, as well as tourmaline boron isotope and crystal chemical data from all three research targets combined with mineralogical observations and various geochemical applications based on lithogeochemical data. Furthermore, U-Pb ages from hydrothermal xenotime and monazite from the Hirvilavanmaa and Naakenavaara deposits are also presented in this work.

The heavily altered host rocks of the atypical Juomasuo Au-Co deposit were classified by utilizing the Zr/TiO_2-Nb/Y immobile element ratio diagram, with recognized lithologies comprising metasedimentary rocks and mafic, intermediate-composition, felsic, and ultramafic meta-igneous rocks. The same diagram was used to determine that protolith composition did not have a significant control on the type or intensity of mineralization. In agreement with petrographic observations from this study and other works, mass-balance calculations revealed that albitization is the oldest alteration event at Juomasuo predating ore formation. Tourmaline associated with the pre-ore albitization has geochemical characteristics common for tourmaline deposited from saline fluids typical of metaevaporitic environments, and it is proposed that saline fluids of an inferred metaevaporitic origin could have been involved in the formation history of the Juomasuo deposit. Molar Element Ratio diagrams and results of principal component analysis reveal that the Co-only and Au-Co ore were mostly deposited during different stages of hydrothermal activity with the former being associated with a chlorite-biotite alteration stage and the latter associated with late sericitization. Results of *in situ* sulfide trace element and sulfur isotope analyses reveal that the two geochemically distinct types of ore formed from distinct fluids. A reduced metamorphic fluid was involved in deposition of the pyrrhotite-dominant Co-rich ore, whereas a relatively oxidized fluid was responsible for deposition of the Au-rich and pyrite-dominant Au-Co ore. Results of this study indicate that the Juomasuo deposit was formed by multiple and spatially coincident hydrothermal processes.

The Hirvilavanmaa Au-only deposit is hosted principally by altered ultramafic metavolcanic rocks. The sulfide mineralogy of the deposit is almost exclusively dominated by pyrite, which locally hosts native Au inclusions. Pyrite is present in quartz-carbonate veins and in their chlorite-rich alteration haloes. Three pyrite generations are distinguished based on their generally low (medians of 0.05, 0.55 and 5.56, respectively) but distinct Co/Ni ratios. The mostly similar trace element geochemistry of all pyrite types indicates that the composition and origin of the hydrothermal fluid involved in ore formation remained relatively constant in all stages of hydrothermal activity. High Co and Ni, and low As contents in pyrite, combined with lithogeochemical characteristics indicate a mafic metavolcanic rock source for the ore-forming components. The generally near-zero distribution of sulfur isotopes (median +1.2‰) from sulfides together with the boron isotope composition of tourmaline gives further support to this model. The major element composition of tourmaline indicates that low fluid/rock ratios and relatively oxidizing conditions prevailed during tourmaline deposition at Hirvilavanmaa.

The atypical Naakenavaara Cu-Co-Ni-Au deposit is primarily hosted by altered metasedimentary rocks, now present as various albitites, mica schists, and phyllites. Ore zones are characterized by sulfide-bearing quartz-carbonate veins that host chalcopyrite, pyrrhotite, and pyrite. The latter two minerals are significant carriers of Co and Ni, with cobaltite being also present locally in Co-rich parts of the deposit. An early base metal-rich mineralizing event started as Co-rich and gradually developed into the main Cu-rich stage of ore formation; two pyrite types with intermediate (mean 12.5) and high (mean 762) Co/Ni ratios, respectively, are associated with these stages. A later and more restricted orogenic Au stage locally overprinted earlier ore zones and deposited pyrite with low (mean 0.3) Co/Ni ratios and a generally distinct trace element geochemistry. Tourmaline crystal chemistry indicates a low fluid/rock ratio and variable redox conditions during the early base metal-rich ore-forming event at Naakenavaara; relatively oxidized conditions prevailed during the pyrite-dominant Co-rich stage, whereas the pyrrhotite- and chalcopyrite-dominant Cu-rich stage is characterized by a shift to more reduced conditions. Results of sulfur isotope analyses from sulfides (median +9.9‰) point towards a metasedimentary source of sulfur at Naakenavaara.

Results of U-Pb dating of hydrothermal xenotime indicate that Co deposition (at 1816 ± 10 Ma) and subsequent Cu deposition (at 1804 ± 3 Ma) in the Naakenavaara deposit took place during a shield-scale event related to late-orogenic Svecofennian tectonism and deformation at c. 1.82-1.80 Ga; hydrothermal activity had also started at Hirvilavanmaa (at 1822 ± 9 Ma) during the same time period. Ages from hydrothermal monazite from Hirvilavanmaa (1785 ± 10 Ma) and Naakenavaara (1752 ± 10 Ma) show that Au deposition took place in both deposits during the waning stages of the Svecofennian orogeny. The 1.82-1.80 Ga and late 1.80-1.75 Ga deformation events were significant for ore formation in all three major greenstone belts of northern Finland, with other studies revealing similar ages of ore formation in deposits from the Central Lapland, Kuusamo and Peräpohja belts.

The recognition of a late orogenic gold stage overprinting earlier base metal-rich ore in the atypical Naakenavaara and Juomasuo deposits fits with observations of other studies from the atypical Rajapalot Au-Co deposit from the Peräpohja belt. Further detailed studies on atypical orogenic gold deposits could help answer if this model is generally applicable to this type of deposits in northern Finland. This study demonstrates that pyrite geochemistry is effective in distinguishing between mineralizing stages and between Au-only and atypical orogenic gold deposits, and that Molar Element Ratios can be used to distinguish between samples that were affected by different stages of hydrothermal activity. These findings can have implications for mineral exploration as these methods could be used to create vectors towards mineralization.

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Espoo, June 2023

Mikael Vasilopoulos

ORIGINAL PUBLICATIONS AND AUTHOR CONTRIBUTION

This thesis is based on the following three research articles submitted to international peer-reviewed journals:

Paper I Vasilopoulos M., Molnár F., O'Brien H., Lahaye Y., Lefèbvre M., Richard A., André-Mayer A.-S., Ranta J.-P., Talikka M., 2021. Geochemical signatures of mineralizing events in the Juomasuo Au–Co deposit, Kuusamo belt, northeastern Finland. Mineralium Deposita 56, 1195–1222. https://doi.org/10.1007/s00126-020-01039-8

Paper II Vasilopoulos M., Molnár F., Ranta J.-P., O'Brien H., 2023. Mineralogical, lithogeochemical and sulfide trace element characteristics of the Hirvilavanmaa Au-only and the base metal-rich Naakenavaara orogenic gold deposits in the Central Lapland belt, northern Finland. Journal of Geochemical Exploration 244, 107132. https://doi.org/10.1016/j.gexplo.2022.107132

Paper III Vasilopoulos M., Molnár F., Ranta J.-P., Kurhila M., O'Brien H., Lahaye Y., Lukkari S., Moilanen M. (submitted for publication) U-Pb geochronology, tourmaline geochemistry, and stable (B, S) isotope constraints from the Hirvilavanmaa Au-only and the polymetallic Naakenavaaara orogenic gold deposits, Central Lapland belt, northern Finland.

The author's contribution to the original research articles is as follows:
Mikael Vasilopoulos is the corresponding author for all the research articles, and he was responsible for most of data collection, for processing and interpretation, and for writing the manuscripts. For article I, drill core logging and sample collection was carried out by the author and Ferenc Molnár, with the help of Mari Kivinen (GTK). Access to drill cores and whole-rock geochemical data was provided by Dragon Mining. Petrography was carried out by the author. Sulfide trace element analyses were conducted by the author under the guidance of Hugh O'Brien. Sulfur isotope analyses were conducted by the author and Ferenc Molnár under the guidance of Yann Lahaye. Processing, analysis, and interpretation of all previously mentioned data was carried out by the author with the help of co-authors. Tourmaline major element and boron isotope analyses and data processing were conducted by Marie Lefèbvre together with Antonin Richard and Anne-Sylvie André-Mayer at Université de Lorraine in France; related data analysis and interpretation were carried out by the author with the help of Jukka-Pekka Ranta. For articles II and III drill core logging and sample collection was carried out by the author together with Ferenc Molnár. Whole-rock geochemical data was provided to the author by the GTK. For article II, sulfide trace element analyses were conducted by the author under the guidance of Hugh O'Brien. Petrographic work was conducted by the author. Data processing, analysis and interpretation were done by the author. For article III, sulfur and boron isotope analyses were done by the author under the guidance of Yann Lahaye. Tourmaline major element analyses were done by the author and Marko Moilanen. SEM-assisted petrography and selection of xenotime and monazite grains for U-Pb isotope analyses was done by the author with the help of Sari Lukkari. The U-Pb isotope analyses and data processing were carried out by the author with the help of Matti Kurhila and Hugh O'Brien. All co-authors helped in editing the text and finalizing the three manuscripts for submission.

CONTENTS

1. INTRODUCTION

The Paleoproterozoic Central Lapland belt (CLB) in northern Finland (Fig. 1) is one of the most significant precious and base metal metallogenic belts in the Fennoscandian Shield, yet its exploration history is relatively short and there is still significant potential for new discoveries (Niiranen et al. 2015; Eilu 2015). Together with magmatic Ni-Cu(-PGE) ore, the most common type of mineralization in the CLB is orogenic gold, as is typical for Precambrian greenstone belts in Finland and globally (Eilu et al. 2007; Eilu et al. 2012; Eilu 2015; Wyche et al. 2015). Approximately half of all known occurrences of orogenic gold in CLB are also significantly enriched in Cu ± Co ± Ni in addition to Au and have been classified as orogenic Au deposits with atypical metal association (e.g., Eilu et al. 2007, 2012; Holma and Keinänen 2007; Holma et al. 2007; Eilu 2015; Fig. 1a). Precise radiometric ages directly related to the formation of orogenic Au deposits in CLB are limited (e.g., Mänttäri 1995; Wyche et al. 2015; Molnár et al. 2017a, 2018, 2019), and new geochronological studies based on a well-established textural context have the potential to reveal important information regarding the age of mineralizing stages in both Au-only and atypical orogenic deposits in the CLB.

The Paleoproterozoic Kuusamo belt (KB) is another metallogenically significant greenstone belt from northern Finland (Fig. 2). The KB contains several epigenetic-hydrothermal Au-Co (±Cu) deposits and occurrences that have been also classified as atypical orogenic gold deposits (Eilu 2015). These polymetallic deposits in the KB have been studied in the past (e.g., Vanhanen 2001), but there are still open questions regarding the processes that led to their formation. The most significant example of Au-Co mineralization is the Juomasuo deposit, with a total mineral resource estimate of 2.37 Mt. Other notable examples include the Hangaslampi, Kouvervaara and Meurastuksenaho deposits.

There has only been limited work so far on the sources of ore-forming components in orogenic Au deposits from the CLB and the KB (Niiranen et al. 2015; Patten et al. 2020, 2023), and detailed studies utilizing geochemical tools such as sulfide trace elements, stable isotopes, and crystal chemistry of tourmaline have the potential to better constrain these sources. An improved understanding of hydrothermal processes leading to formation of Au-only and atypical orogenic gold deposits in these areas is needed in order to support exploration for the discovery of new deposits. The added knowledge concerning especially the atypical base metal-rich deposits can have implications for exploration on a global scale, as similar deposits are also found in several terranes outside of Finland (e.g., Slack 2013).

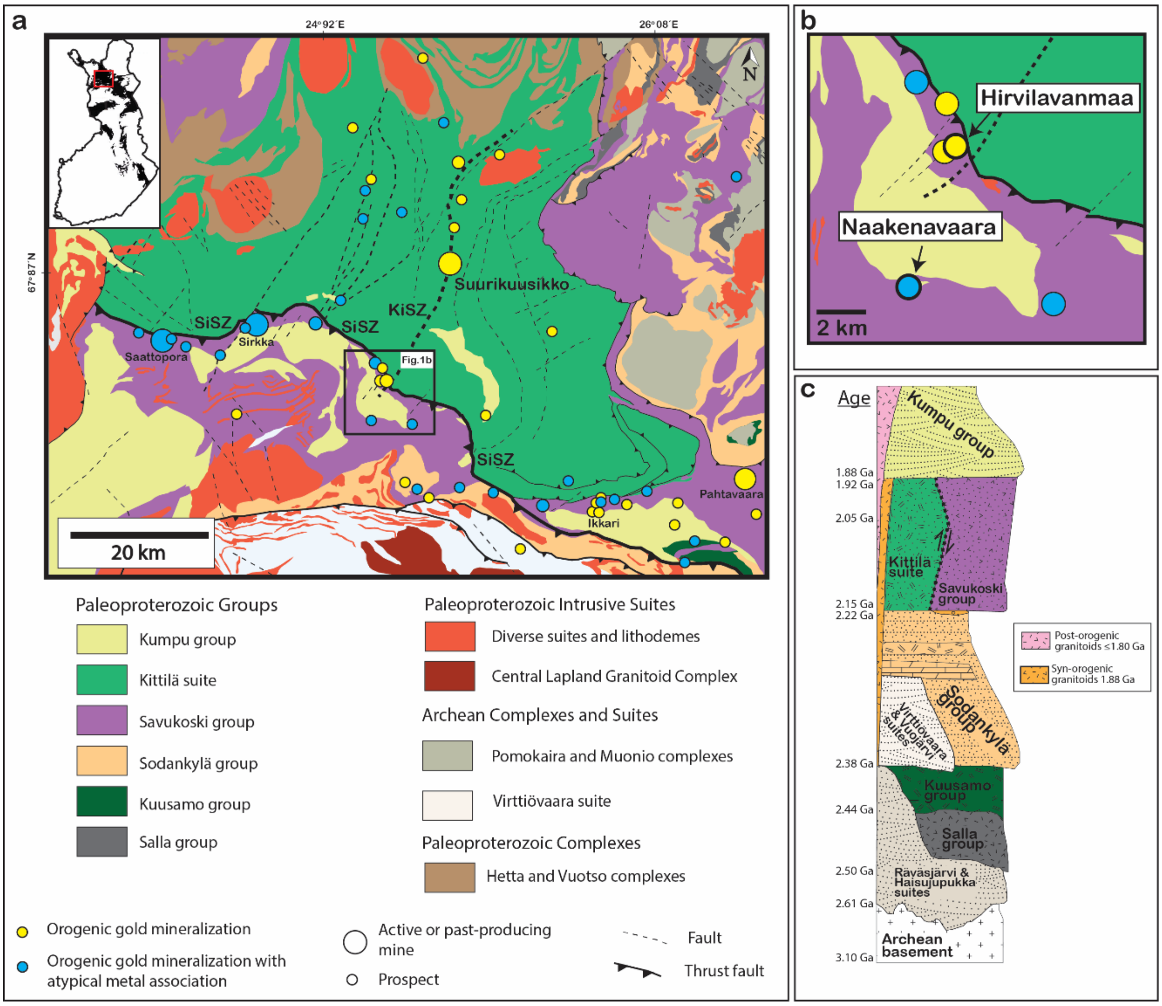


Figure 1. (a) Simplified geological map of Central Lapland belt (CLB) showing location of discovered Au-only (yellow circles) and atypical base metal-rich (blue circles) orogenic Au deposits and occurrences. Inset map shows the position of CLB in Finland. (b) Detailed view of marked area from Fig. 1a, showing location of the Hirvilavanmaa and Naakenavaara deposits. (c) Stratigraphic column of CLB, modified after Köykkä et al. (2019). Figure taken from Vasilopoulos et al. (2023)

The main objective of this doctoral dissertation is to apply multiple geochemical methods, combined with mineralogical observations, on Paleoproterozoic orogenic Au deposits with different metal associations from northern Finland with an aim of understanding the evolution of hydrothermal processes that resulted in their formation. The three research targets chosen for this dissertation are the Juomasuo Au-Co deposit from the Kuusamo belt, and the Hirvilavanmaa Au-only and

Naakenavaara Cu-Co-Ni-Au deposits from the Central Lapland belt. All three deposits have been classified as orogenic, with Hirvilavanmaa representing a classic Au-only orogenic deposit and Juomasuo and Naakenavaara representing examples of atypical, base metal-rich orogenic mineralization. This work presents results of mineralogical-petrographical studies combined with *in situ* sulfide trace element and sulfur isotope analyses, as well as tourmaline boron isotope and crystal chemical characteristics from all three research targets, together with geochemical applications based on lithogeochemical data. Precise U-Pb ages from hydrothermal xenotime and monazite are also presented in this work in order to constrain the timing of ore formation in Au-only and atypical orogenic gold deposits during the tectonic evolution in the CLB.

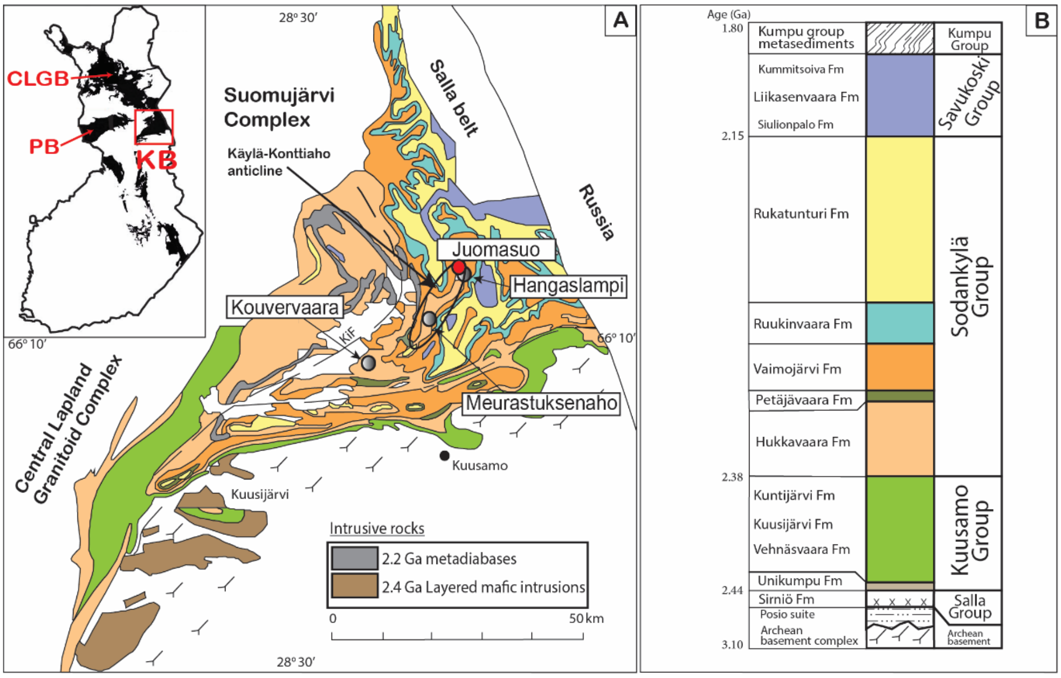


Figure 2. a) Simplified geological map of Kuusamo belt (KB) showing the location of the Juomasuo Au-Co deposit. Inset map shows the position of the KB, Peräpohja bel (PB) and Central Lapland belt (abbreviated as CLGB in this figure). b) Stratigraphic column of KB. Figure modified from Vasilopoulos et al. (2021).

2. GOLD-RICH MINERAL DEPOSITS IN METAMORPHIC TERRANES

2.1 Orogenic gold deposits

Orogenic gold deposits are one of the most economically important mineral deposit types in Precambrian greenstone belts (e.g., Groves et al. 2003; Goldfarb et al. 2005; Huston et al. 2012), and one of the most important gold deposit types in general. These epigenetic-hydrothermal deposits are formed by complex large-scale processes that include the mobilization of metal-rich fluids through the Earth's crust, and the precipitation of metals in structurally controlled localities (e.g., Large et al. 2011; Goldfarb and Groves 2015). They show a wide range of formation depths (5-20 km) and P-T conditions (0.5-5 kbars; 200-650 °C) and are typically hosted by greenschist facies metamorphic rocks; some significant examples of orogenic gold mineralization are also found in higher-grade rocks (e.g., Groves et al. 2003; Goldfarb and Groves 2015). Their formation typically takes place during late to post-peak metamorphic events at accretional and collisional tectonic settings (Goldfarb and Groves 2015).

Orogenic gold deposits have formed over an exceptionally large time span from the Paleoarchean to the Tertiary and in most cases show consistency in chemical composition (Goldfarb and Groves 2015). They are typically formed from low- to moderate-salinity (3-7 wt% NaCl eq.) H_2O-CO_2-CH_4-N_2-H_2S fluids. The ore bodies are commonly vertically extensive, and in most cases, gold is the only metal enriched in economically significant concentrations. Gold is hosted in quartz (± carbonate) veins and in sulfidized wall rocks typically in second or third order structures. The sources of metal, ligands, and fluids that are involved in formation of orogenic gold deposits are still debated (Goldfarb and Groves 2015; Groves et al. 2019; Goldfarb and Pitcairn 2023). Proposed models include the metamorphic devolatilization of supracrustal rocks (e.g., Pitcairn et al. 2006; Phillips and Powell 2010; Tomkins 2010; Large et al. 2011; Patten et al. 2020, 2023), the subcontinental lithospheric mantle (Groves et al. 2019), and magmatic sources (e.g., Burrows et al. 1986; Masurel et al. 2019), although the latter model is considered fairly controversial (Goldfarb and Pitcairn 2023).

In Finland, orogenic gold deposits are found in both Archean and Proterozoic greenstone and schist belts (Eilu 2015). The most significant example of orogenic gold mineralization is the Suurikuusikko deposit in the Central Lapland belt (CLB), which is currently the largest gold producer in Europe (Agnico Eagle 2020). The potential for new orogenic gold discoveries in Finland is highlighted by the recent discovery of the Ikkari deposit in CLB, with an inferred gold resource estimate of 4.25 Moz (Rupert Resources 2022).

2.2 Orogenic gold deposits with atypical metal association

A category of peculiar epigenetic-hydrothermal gold-bearing deposits that are also enriched in base metals occur in some provinces dominated by orogenic gold deposits and are termed as orogenic gold deposits with an atypical metal association (e.g., Goldfarb et al. 2001; Groves et al. 2003). In Finland, deposits classified as orogenic with atypical metal association can be found in the Kuusamo, Central Lapland, and Peräpohja belts (Eilu 2015). These deposits have important similarities with classic Au-only orogenic deposits, with the most significant difference being in the enrichment of base metals in addition to gold.

Examples of atypical base metal-rich gold deposits can be found in different metamorphic terranes globally, with prominent examples including the deposits in the Idaho cobalt belt (Slack 2012), the Skutterud deposit in Norway (Grorud 1997), and the Werner Lake (Pan and Therens 2000) and NICO (Goad et al. 2000) deposits in Canada. The most important recent discovery of this type of deposits in Finland is the Rajapalot Au-Co deposit in the Perapohja belt (e.g., Ranta et al. 2021; Raič et al. 2022). Proposed models that could explain the genesis of such atypical orogenic deposits include the mobilization of exceptionally saline basinal fluids under moderate to high-metamorphic conditions prior to the orogeny (e.g., Yardley and Graham 2002; Yardley and Cleverley 2013; Qiu et al. 2021), and the overprinting of an existing base metal-rich deposit by later orogenic gold mineralization through the reactivation of the same structures during subsequent events (Groves et al. 2003; Vasilopoulos et al. 2021; Ranta et al. 2021; Raič et al. 2022).

3. REGIONAL GEOLOGY OF THE RESEARCH AREAS

In northern Finland, the Fennoscandian shield consists of an Archean core and Proterozoic crustal cover. The Archean domains of the shield are divided into four major provinces, namely the Karelian, Belomorian, Kola, and Norrbotten provinces (e.g., Lahtinen 2012). The Archean evolution of Fennoscandia started at ca. 3.5-3.2 Ga and continued through several accretion events until the 2.5-2.1 Ga rifting of the Archean supercontinent, and subsequent evolution of a passive margin along the SW and S edges of the craton (Lahtinen et al. 2005; Köykkä et al. 2019). The main Paleoproterozoic orogenic evolution took place between 1.92-1.78 Ga and is divided into the Svecofennian and Lapland-Kola Orogens (e.g., Lahtinen et al. 2018). The Paleoproterozoic supracrustal cover of northern Finland can be divided into the Central Lapland, Kuusamo and Peräpohja belts. The research targets in this study are situated in the former two belts, and more detailed geological features of these belts are presented in this chapter.

3.1 Kuusamo belt

Rocks comprising the Paleoproterozoic Kuusamo belt (KB) are part of Karelian supracrustal formations with ages between 2.4 to 1.9 Ga (Silvennoinen 1972, 1992; Huhma et al. 2018).

Formation of the KB took place at least partially in an intracratonic failed rift setting related to the Paleoproterozoic breakup of the Archean Karelian craton (Hanski and Huhma 2005). The total thickness of the lithological sequence in the KB varies from 5 to 7 km (Lahtinen and Köykkä 2020), and includes several formations of volcanic and sedimentary origin, including the products of three stages of mafic volcanism (Pankka 1992). The stratigraphy of the KB was first defined by Silvennoinen (1972, 1991) and has been recently refined by Huhma et al. (2018), Köykkä et al. (2019) and Lahtinen and Köykkä (2020). The stratigraphy of the KB includes several formations belonging to the Salla, Kuusamo, Sodankylä, Savukoski and Kumpu groups (Fig. 2b). The Posio suite, the Unikumpu, Hukkavaara, Vaimojärvi and Rukatunturi formations, as well as the units belonging to the Savukoski and Kumpu groups are dominated by metasedimentary rocks. The Sirniö Formation consists of principally felsic metavolcanic rocks and the Vehnäsvaara, Kuusijärvi, Kuntijärvi, Petäjävaara and Ruukinvaara formations are the products of predominantly mafic volcanism.

Rocks of the KB were subjected to deformation and regional metamorphism during the Svecofennian orogeny (Silvennoinen 1972, 1992; Lahtinen and Köykkä 2020). Deformation took place in several stages, starting with an E-W compressional phase (D1), followed by N-S shortening (D2) and two overprinting stages of folding (D3 and D4); KB was also locally affected by a late D5 overprint with a more brittle character, although there are still open questions regarding the importance of this stage (Lahtinen and Köykkä 2020). Metamorphic grades in the KB vary from greenschists facies in the south and centre of the KB to higher metamorphic grades (up to medium-pressure amphibolite facies) in the western, eastern and northern parts of the belt (Hölttä and Heilimo 2017; Lahtinen and Köykkä 2020). In the central part of the KB, the NE-trending F2 Käylä-Konttiaho anticline is associated with the majority of significant Au-Co occurrences in the KB, including the Juomasuo Au-Co deposit (Fig. 2a). Results of Re-Os and U-Pb geochronological studies indicate that Au-Co mineralization in the KB formed by multiple hydrothermal processes during the late stages (1.81-1.76 Ga) of the Svecofennian orogeny, postdating regional peak metamorphism (Pohjolainen et al. 2017; Molnár et al. 2020).

3.2 Central Lapland belt

The supracrustal evolution of the CLB spanned from the early Paleoproterozoic (~2.44 Ga) intracontinental rifting of the Archean basement, through a prolonged basin evolution stage that was terminated by the onset of the Svecofennian orogeny at around 1.92 Ga (Korja et al. 2006; Lahtinen et al. 2005). The stratigraphy of the CLB includes six main lithostratigraphic groups and several minor suites and lithodemes (Fig. 1c). During the repeated intra-continental and continental margin rifting of the Archean basement (ca. 2.5-2.1 Ga) the principally felsic- to intermediate, and tholeiitic- to komatiitic metavolcanic rocks of the Salla and Kuusamo Groups, respectively, were deposited (Köykkä et al. 2019). Subsequent syn-rift to post-rift stages led to deposition of sedimentary and mafic volcanic rocks of the Sodankylä Group. The post-rift stage (ca. 2.1-1.92 Ga) resulted in deposition of Savukoski Group and the Kittilä suite (Köykkä et al. 2019). The former Group comprises phyllites and graphite- and sulfide-bearing black schists, and komatiitic and picritic metavolcanic rocks. The allochthonous Kittilä suite overlies rocks of the Savukoski Group and comprises mostly tholeiitic basalts with subordinate felsic intrusions, banded iron formations, and various metasedimentary packages. The final foreland basin stage resulted in deposition of sediments and syngenetic felsic volcanic rocks of the Kumpu Group (Köykkä et al. 2019). The Paleoproterozoic supracrustal rocks were intruded at 2.44 Ga and 2.05 Ga by mafic-ultramafic layered intrusions (e.g., the Koitelainen and Kevitsa igneous complexes) and at 1.88-1.76 Ga by syn- to post-orogenic granitoids (Nironen 2005; Patison 2007; Köykkä et al. 2019).

The CLB has been affected by several stages of ductile deformation and metamorphism during the 1.92-1.77 Ga Svecofennian orogeny, followed by a final stage of brittle deformation (Lahtinen et al. 2005, 2015; Patison 2007; Sayab et al. 2019). The central part of the CLB that hosts most of the discovered Au deposits (Fig. 1a) is characterized by greenschist facies metamorphic grade, and it is bound on all directions by mid-amphibolite facies rocks (Hölttä and Heilimo 2017). The general consensus is that peak metamorphism in the CLB took place at ca. 1.88-1.86 Ga (Lahtinen et al. 2015; Hölttä and Heilimo 2017). Two peaks in formation of orogenic Au mineralization in the CLB have been identified: (1) during early collision and ductile deformation (ca. 1.92 Ga; Lahtinen et al. 2012; Wyche et al. 2015; Molnár et al. 2017a, 2018) and (2) during late- to post orogenic hydrothermal events (ca. 1.83-1.76 Ga; Patison 2007; Molnár et al. 2017a, 2018).

4. DESCRIPTION OF RESEARCH TARGETS

4.1 Geology and exploration history of the Juomasuo Au-Co deposit

Exploration in the Kuusamo area started in the late 1950s when Finnish companies Suomen Malmi Oy and Outokumpu Oy started exploring the region. Exploration for Au, Fe, and U continued in the area, and in the late 1970s, the Geological Survey of Finland (GTK) started exploration and research activities in the area that continued up to date. The Juomasuo deposit was discovered in 1985 by airborne magnetic and electromagnetic surveys. The exploration permit has changed ownership several times, but apart from open pit test mining, no actual mining has taken place as of yet.

The Juomasuo deposit is situated in the northern part of the 25-km long Käylä-Konttiaho anticline in an area that hosts several Au-Co occurrences (Fig. 2a). The mineralized zone consists of one major lode with known surface dimensions of 50 x 100 m, and several smaller sulfidized zones that are situated near the main ore body within an area of approximately 0.5 km^2 (Vanhanen 2001). The main lode has been drilled to a depth of 300 m and is continuous to that level; the lode dips to the SW at an average of 50 degrees. The Juomasuo deposit hosts two main types of ore, Co ore and Au-Co ore (Pankka 1992; Witt et al, 2020; Vasilopoulos et al. 2021). The total mineral resource estimate is 2.37 Mt grading 4.6 g/t Au and 0.13 wt% Co, and an additional 5.04 Mt of Co resources (accompanied by variable low-grade Au concentrations) grading 0.12 wt% Co (Dragon Mining 2014). Apart from Au and Co, common trace metals in the deposit include Cu, Mo, and REE, together with local U enrichment (Vanhanen 2001).

Pervasive albitization widely affected the rocks in the Juomasuo area. Mineralized zones in the deposit also contain quartz, chlorite, biotite, sericite, carbonate, amphibole, and talc in addition to albite (Vanhanen 2001; Witt et al. 2020). Pyrrhotite is the most common sulfide in the deposit, followed by pyrite. The Co ore is pyrrhotite-rich, whereas the Au-rich ore lenses are locally pyrite-dominated (Witt et al. 2020). Noteworthy accessories in the ore include chalcopyrite, cobaltite, cobaltpentlandite, molybdenite, rutile, magnetite, native Au, tellurides, and local scheelite and uraninite (Vasilopoulos et al. 2021).

4.2 Geology and exploration history of the Hirvilavanmaa Au deposit

The Hirvilavanmaa Au deposit is situated approximately 15 km northeast from the town of Kittilä in the southern part of the CLB (Fig. 1a). The area around Hirvilavanmaa was first studied by GTK in the 1980s and several mineralized zones, including Hirvilavanmaa, were discovered (e.g., Keinänen et al. 1988; Keinänen 1994). The currently known NNE-trending mineralized domain is 270 m long and 90 m wide and includes narrow lens-like mineralized bodies dipping at 85 degrees. Recent drilling has indicated that the mineralized zone extends beyond previously set limits remaining open at depth and along strike to the north (Rupert Resources 2020).

Hirvilavanmaa is hosted mainly by intensely altered and deformed ultramafic metavolcanic rocks of komatiitic affinity. The komatiite unit now appears as an assemblage of schists, and albite- and carbonate- dominant rocks. Other formations in the Hirvilavanmaa area include sulfide- and graphite-bearing schists, quartzites and mafic metavolcanic rocks, with minor amounts of the latter being present in the host sequence of the deposit (Hulkki and Keinänen 2007). The earliest alteration stages that predate ore formation at Hirvilavanmaa include talc, carbonate, and albite alteration; Hulkki and Keinänen (2007) also recognized early regional chlorite alteration that predates Au mineralization. Hydrothermal processes associated with ore formation resulted in formation of quartz-carbonate veins, abundant chlorite alteration that typically forms alteration haloes adjacent to the veins, and late more intense carbonate alteration (Vasilopoulos et al. 2023). Pyrite is hosted in the quartz-carbonate veins or in their chlorite-rich alteration haloes that locally also host abundant tourmaline. Pyrite almost exclusively dominates the sulfide mineralogy in the deposit and locally contains native Au inclusions. Hematite and magnetite are present as accessories in the distal parts of the ore zones. No other metals are significantly enriched apart from Au in the deposit.

4.3 Geology and exploration history of the Naakenavaara Cu-Co-Ni-Au deposit

The polymetallic Naakenavaara deposit is situated just over 5 km SSW from Hirvilavanmaa (Fig. 1b). The surroundings of the Naakenavaara area were first studied by the GTK in the 1970s when an airborne geophysical survey detected an electrical anomaly caused by graphite- and sulfide-bearing phyllite. At the time, Naakenavaara was characterized as a potentially economic Cu deposit (Nenonen 1975). Exploration by the GTK continued in the 1990s after elevated Au concentrations were discovered by reanalysing old drill cores (Keinänen 2002). The most recent exploration activity took place in the 2010s. The precise shape and extent of the ore zones have not yet been defined but results of drilling indicate that there are several lodes in the northern and southwestern parts (~2 km apart) of the geophysical anomaly.

The Naakenavaara Cu-Co-Ni-Au deposit is hosted primarily by altered metasedimentary rocks that appear as various mica schists, phyllites, and albitites. Comparatively minor amounts of ultramafic and mafic metavolcanic rocks are also present in the host sequence, with the latter being more abundant in the less extensively drilled southwestern part of the Naakenavaara area. Rock units have a subhorizontal to horizontal setting in a very low-angle antiform; intense fracturing has led to brecciation of host rocks.. Pre-ore albitization affected the metasedimentary host rocks at Naakenavaara to a various degree; pervasively albitized quartzites typically form the uppermost lithological unit at Naakenavaara. Ore zones are principally hosted in phyllite, graphite phyllite and sericite schists, with the latter rock type being especially sulfide-rich (Keinänen 2002). In addition to abundant sericite, ore zones locally contain biotite, chlorite and carbonate minerals. Sulfide-bearing quartz-carbonate veins are hosted in intensely fractured zones. Ore mineralogy is dominated by chalcopyrite, pyrrhotite and pyrite; they occur principally in quartz-carbonate veins but are also present as fine dissemination in wall rocks surrounding them. Cobaltite is also found in Co-rich parts of the deposit. Copper is the most evenly enriched metal in the deposit, with the main type of ore characterized by Cu (± Au) enrichment. Zones of significant Co (± Au) enrichment mark the second type of ore that is less widespread in the deposit. The best Cu intercepts exceed 1.7 wt%, with Co and Ni concentrations reaching up to 0.3 wt% and 0.5 wt%, respectively. Gold concentrations are generally low, but locally reach up to 10 ppm (Vasilopoulos et al. 2023).

5. ANALYTICAL METHODS

Lithogeochemical data used in article I were provided by Dragon Mining Ltd. Whole-rock chemical analyses were done by ALS Global Ltd. at their laboratories in Rosia Montana, Romania, and Vancouver, Canada, during 2011. Lithogeochemical data used in article II were provided by the GTK. Whole-rock analyses were done at the geochemical laboratory of the GTK between 1988 and 1996. More detailed descriptions of the analytical methods used for the whole-rock analyses, as well as for the software used for data processing can be found in articles I and II (Vasilopoulos et al. 2021, 2023).

Trace element analyses from pyrite, pyrrhotite and chalcopyrite for articles I and II and sulfur isotope analyses for articles I and III were done by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) at the Finnish Geosciences Research Laboratories, GTK, Espoo. For the sulfide trace element analyses, the laser beam diameter was 50 μm with a pulse frequency of 10 Hz and fluence of 2.5 J/cm^3. Sulfur isotope analyses were done at medium resolution (ΔM/M = 3000) with a laser beam diameter of 40 μm using a fluence of 3.5 J/cm^3 at 3 Hz frequency.

Tourmaline major element analyses for articles I and III were acquired by means of electron probe micro-analyzers (EPMA) at the GeoRessources laboratory, Université de Lorraine, Nancy, and the Centre for Material Analysis, University of Oulu, respectively. Boron isotope composition of tourmaline for article I was measured *in situ* by means of a secondary ion mass spectrometer (SIMS) at the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy. Boron isotope analyses of tourmaline from article III took place at the Finnish Geosciences laboratories by means of LA-ICP-MS.

The U-Pb geochronological study of monazite and xenotime for article III took place at the Finnish Geosciences laboratories, GTK, Espoo. Monazite and xenotime were located in polished thin sections by means of a JEOL JSM5900LV (SEM). U-Pb dating analyses were done using a Nu Plasma Attom single collector ICP-MS connected to a Photon Machine Excite laser ablation system with a 15 μm beam size, a pulse frequency of 5 Hz, and beam energy density of 2.17 J/cm^3. More detailed description of the analytical procedure can be found in article III.

6. REVIEW OF RESEARCH ARTICLES

6.1 Overview

This doctoral dissertation is based on three research articles submitted for publication to internationally acclaimed peer-reviewed scientific journals.

Article I presents mineralogical, lithogeochemical, sulfide trace element and sulfur isotope, as well as tourmaline crystal chemical and boron isotope data from the Juomasuo Au-Co deposit in the Kuusamo belt. The aim of the study was to utilize diverse geochemical data backed by petrographic observations, in order to understand the temporal relationship between Co and Au deposition, the relationship of metal enrichment with protolith composition and alteration mineralogy, and whether Au and Co in the deposit were deposited from a single fluid.

Article II presents mineralogical, lithogeochemical and sulfide trace element data from the Hirvilavanmaa (Au-only) and the atypical base metal-rich Naakenavaara orogenic gold deposits from the Central Lapland belt. The main objective of this study was to compare formation conditions and understand the origin of differences in the metal associations of these two deposits, and to investigate if the deposits had been correctly classified as members of the orogenic gold deposit clan.

Article III builds up on the previously gathered information from Article II and utilizes the same samples with well-known mineralogical, lithogeochemical, and sulfide trace element characteristics to constrain the temporal evolution of hydrothermal processes and better understand the origin of ore-forming components. To achieve these objectives, precise U-Pb ages from LA-ICP-MS analyses of hydrothermal xenotime and monazite are presented together with crystal chemical and boron isotope data from tourmaline, and sulfur isotope data from sulfides.

6.2 Article I

Geochemical signatures of mineralizing events in the Juomasuo Au–Co deposit, Kuusamo belt, northeastern Finland.

Mikael Vasilopoulos, Ferenc Molnár, Hugh O'Brien, Yann Lahaye, Marie Lefèbvre, Antonin Richard, Anne-Sylvie André-Mayer, Jukka-Pekka Ranta, Matti Talikka, 2021

Mineralium Deposita 56, 1195–1222

Based on drill core logging supported by whole rock geochemical data the intensely altered host rocks at Juomasuo comprise principally metasedimentary rocks and various meta-igneous rocks. The Immobile Element Ratio diagram of Pearce (1996) was used for classifying the host rocks at Juomasuo and to investigate if the lithology in general played a role in controlling metal enrichment. Recognized host rocks at Juomasuo include metasedimentary rocks, mafic, intermediate-composition, and felsic metavolcanic rocks, and an ultramafic sill (Fig. 3). By plotting Au and Co grades in the same Immobile Element Ratio diagram it was established that lithology did not play a major role in controlling the Au- and Co-enrichment as enrichment of both metals is similar in terms of its extent and grades in all rock types, with the exception of the generally barren ultramafic sill (Fig. 3).

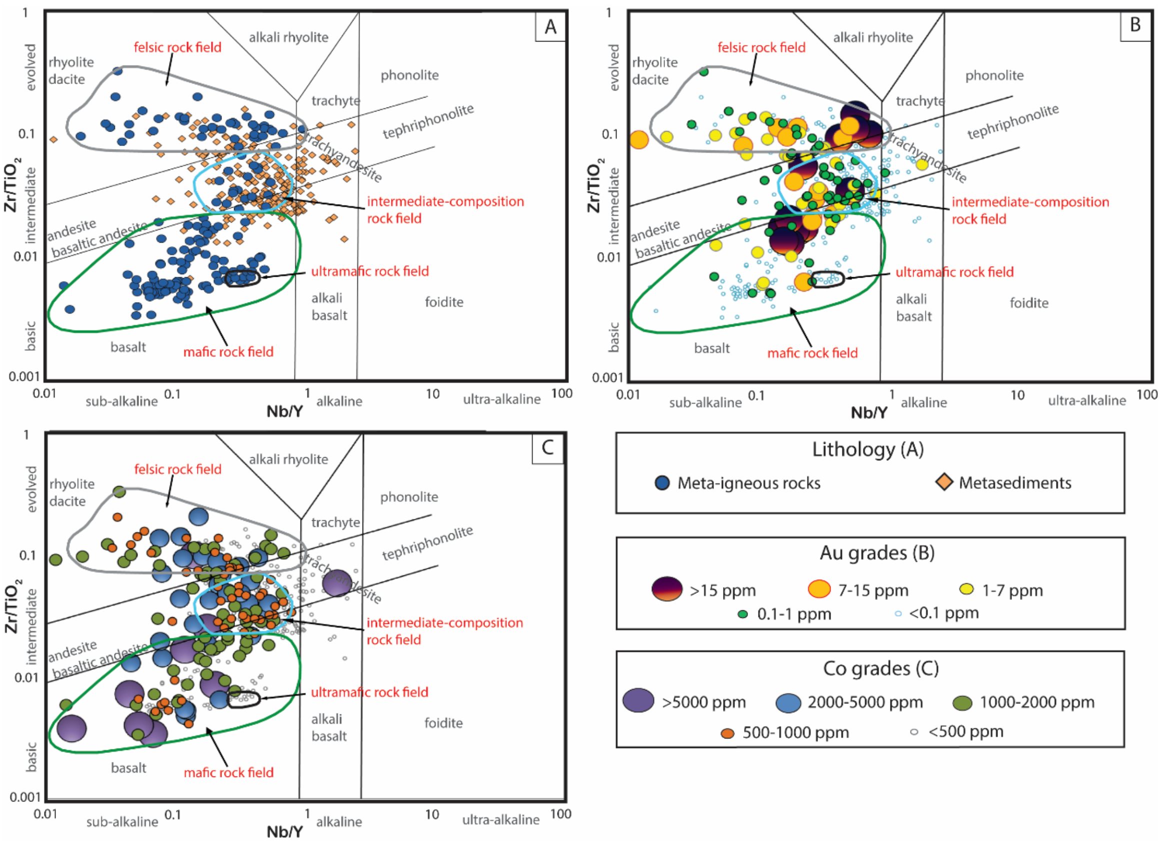


Figure 3. (A) Whole-rock data for samples from Juomasuo divided into meta-igneous and metasedimentary rocks and plotted on the Nb/Y-Zr/TiO_2 diagram of Pearce (1996; after Winchester and Floyd 1977). Metasedimentary rocks do not have a separate field as they are a mixture of both felsic and mafic components. (B) All studied rock samples from Juomasuo categorized according to Au grades. (C) All studied rock samples from Juomasuo categorized according to Co grades. Figure taken from Vasilopoulos et al. (2021).

Petrographic observations indicate that the pervasive albitization that affected the host rocks at Juomasuo was the first alteration stage in the deposit and it was followed by a chlorite (± biotite ± amphibole) alteration stage and finally a sericite alteration stage. Based on mass-transfer calculations albitization predated the Au-Co mineralization, as Na contents decrease in intervals hosting Au and Co mineralization compared to the least altered samples for all examined host rock types.

The Juomasuo deposit contains two types of ore: Co-only ore and Au-Co ore. Pyrrhotite is the most common sulfide mineral in most parts of the mineralized zones, followed by pyrite; the latter is locally more abundant in parts of the Au-Co ore. . Co-rich parts of the ore also host cobaltite and cobaltpentlandite, (as flame-like exsolutions in pyrrhotite). Other notable accessory minerals in the ore zones include molybdenite, rutile, magnetite, tellurides, scheelite, native Au, and uraninite.

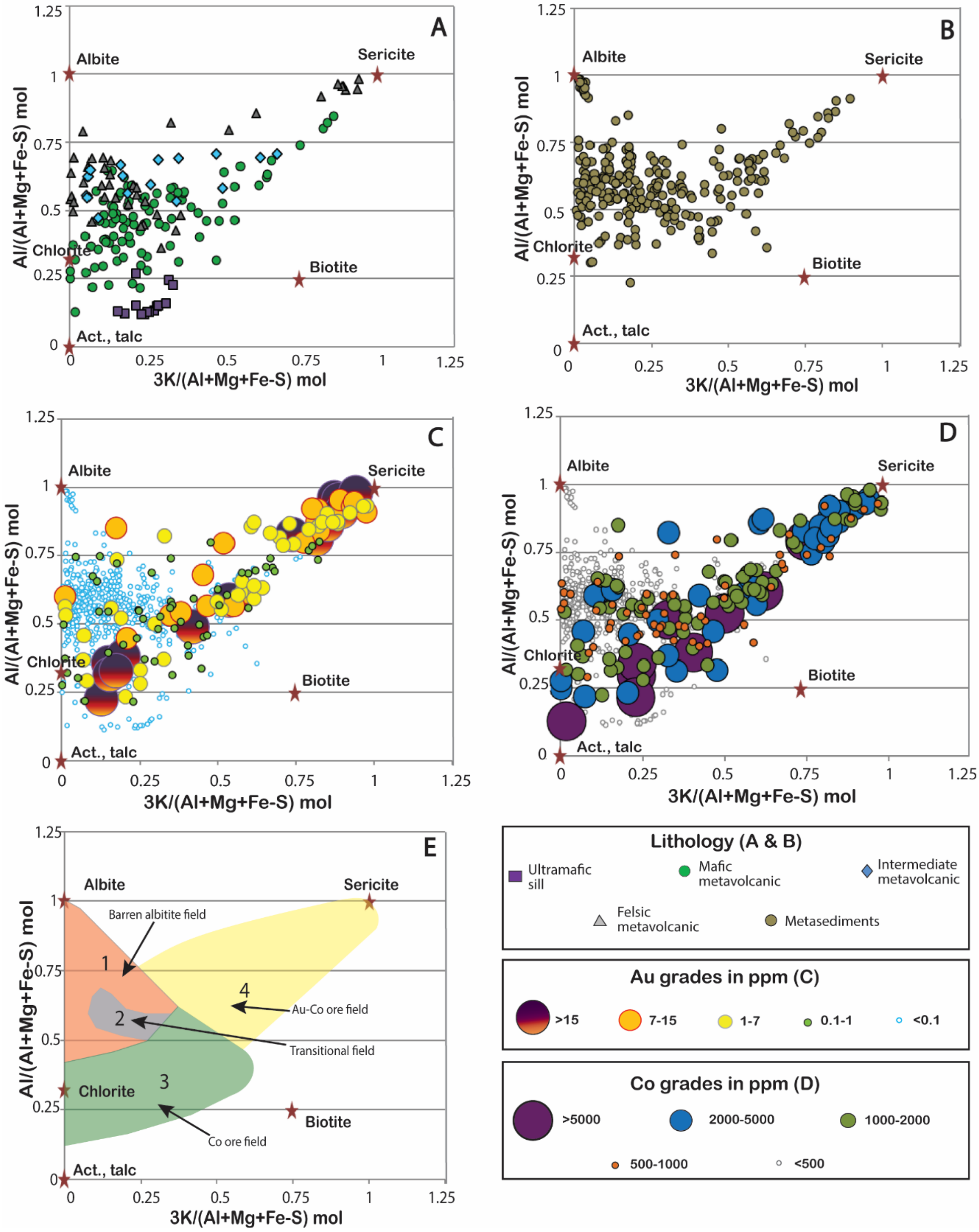


Figure 4. Molar Element Ratio (MER) diagrams showing effects major alteration minerals to rock types at Juomasuo. (a) MER diagram for different meta-igneous rock types. (b) MER diagram for metasedimentary rocks. (c) MER diagram for all Juomasuo rock samples categorized according to Au grades. (d) MER diagram for all Juomasuo rock samples categorized according to Co grades. (e) MER diagram with four fields based on clustering of compositional data for barren and mineralized samples from Juomasuo; field 1: barren albitite field; field 2: transitional field; field 3: Co ore field; field 4: Au-Co ore field. Figure taken from Vasilopoulos et al. (2021).

The effect of the different alteration types on different host rocks were examined with the use of Molar Element Ratio (MER) diagrams. Based on the prominent alteration minerals in the deposit the 3*K/(Al+Mg+Fe-S) and Al/(Al+Mg+Fe-S) ratios were chosen for the axes of the diagram as they best represent the major alteration minerals (albite, chlorite, biotite, sericite) and allocate them with distinct places in the MER diagram (Fig. 4a-b). All rock types, except for the ultramafic sill, were affected by various degrees of albitization, with metasedimentary rocks being the most intensely albitized rock type. Subsequent chlorite, biotite, and sericite alteration affected most rock types (Fig 4a-b). The barren ultramafic sill stands out from the other rock types as it lacks albitization and sericitization (Fig. 4a). The same MER diagram was also used for examining the relationship between hydrothermal alteration and Au- and Co-enrichment by categorizing rock samples according to their Au and Co grades (precise values for each class of Au and Co grades can be found in the legend of Figure 4). Most Co-rich samples (including the highest Co grades in the deposit exceeding 0.5 wt% Co) plot in the lower portion ($y < 0.5$) of the MER diagram in an area that is closely associated with chlorite-biotite alteration; many of these samples have no significant Au enrichment and are thus part of the Co-only ore. This indicates that the chlorite-dominant alteration event was closely associated with enrichment of Co at Juomasuo. Part of the Co-rich samples also plot close to the sericite end member; these rock samples also host most of the significant Au concentrations indicating that most of the Au enrichment (along with some Co) was closely associated with sericite alteration (Fig. 4c). Results of principal component analysis (PCA) on whole-rock geochemical data also support deposition of Co-only and Co-Au ore mostly in different mineralizing stages, as PCA vectors of Co and Au are perpendicular indicating no correlation between them.

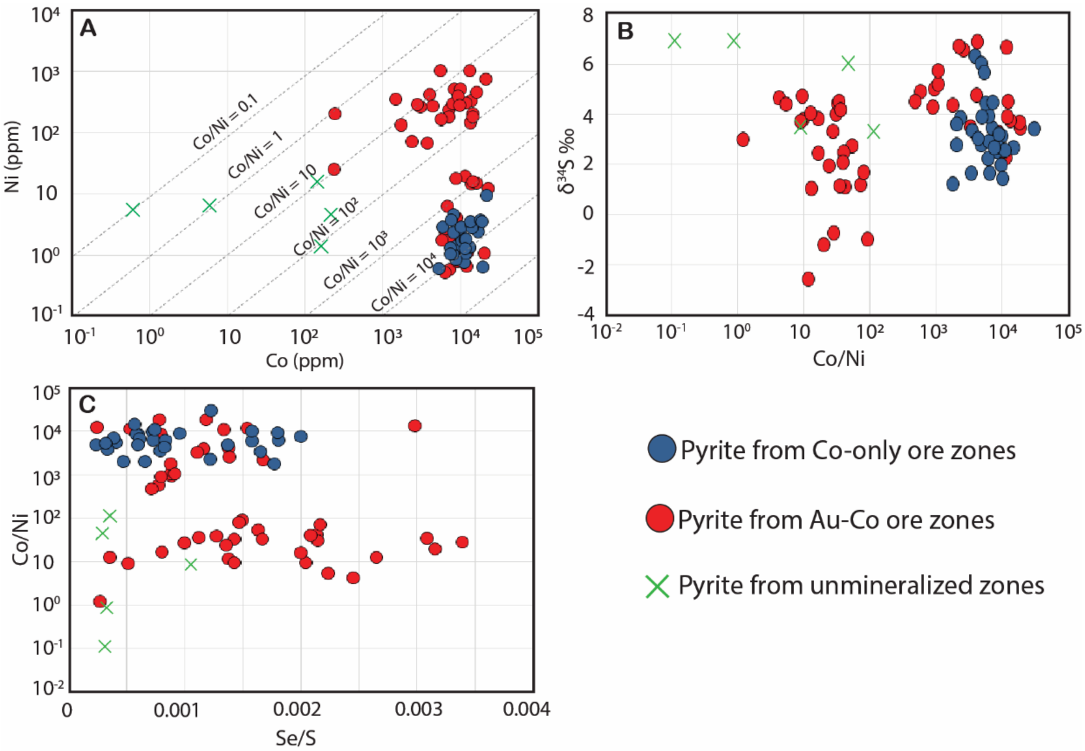


Figure 5. (A) Co vs. Ni scatterplot diagram for pyrite from Juomasuo. Lower cluster with high Co/Ni ratios includes pyrite associated with chlorite and deposited during the Co-rich stage. Pyrite in the upper cluster includes pyrite associated with sericite and deposited during the subsequent Au-rich stage. (B) Co/Ni vs. $\delta^{34}S$ scatterplot diagram for pyrite from Juomasuo. Figure modified from Vasilopoulos et al. (2021)

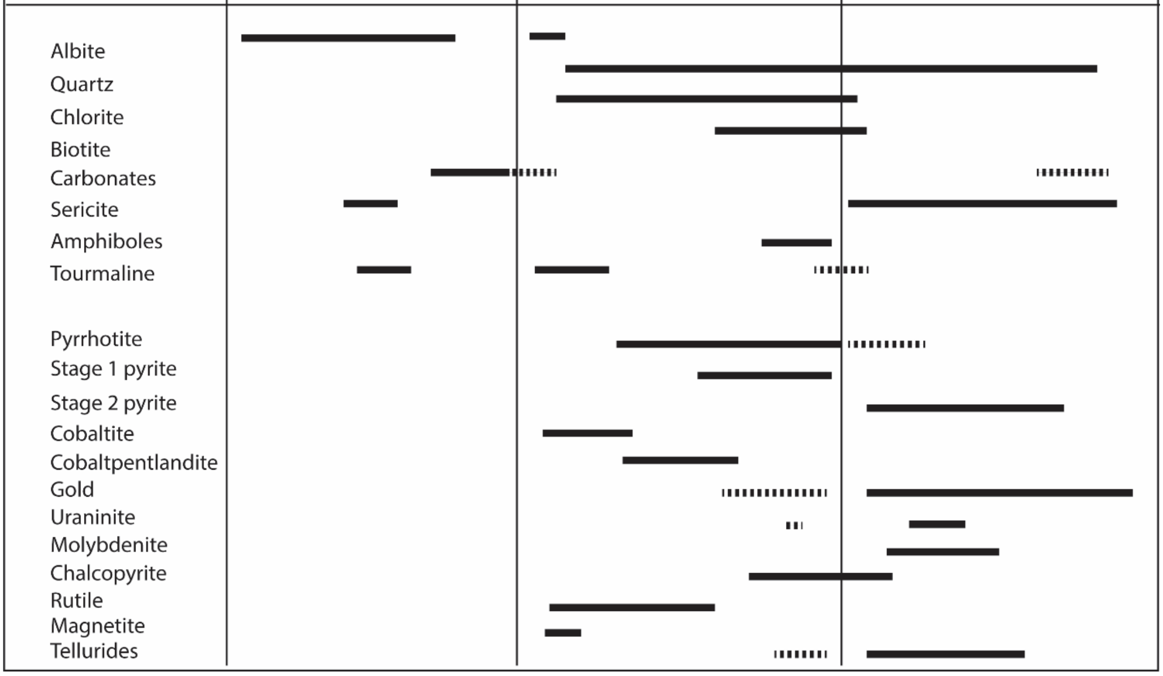
Two pyrite generations with distinct trace element and sulfur isotope characteristics are associated with the two mineralizing stages at Juomasuo. Pyrite which deposited during the early Co-rich stage has particularly high Co/Ni ratios (mostly > 1000; Fig. 5a), a relatively narrow range of Se/S ratios (Fig. 5c; mean 1×10^{-3}) and sulfur isotope values with the latter having a mean $\delta^{34}S$ of +3.8‰ (Fig. 5b). These characteristics indicate that the origin and chemistry of the fluid remained relatively constant throughout the Co-rich mineralizing stage; based on the dominance of pyrrhotite, relatively reduced conditions prevailed during this stage. Pyrite deposited during the late Au-rich stage, on the other hand, has significantly lower Co/Ni ratios (< 100; Fig. 5a), a wider range of Se/S ratios (Fig. 5c; mean 1.7×10^{-3}) and a mean $\delta^{34}S$ of +2.4‰ (Fig. 5b); sulfur isotope data in this type of pyrite also include several negative values. These characteristics, together with the enrichment of redox-sensitive elements such as Ni and Te (cf. Brugger et al. 2016) and the dominance of pyrite during the late Au-rich stage, indicate that a different and more oxidizing fluid, compared to the earlier Co-rich stage, was involved in this mineralizing stage. The involvement of distinct fluids in the two mineralizing stages is also supported by differences in several other trace element compositions between the two pyrite types.

Several different tourmaline types were recognized at Juomasuo. Tourmaline type 1 is associated with pre-ore albitization, whereas subtype 1b includes part of type 1 tourmaline cores with a distinct chemical composition. Types 2, 3, and 4 are hosted in samples that have been affected by subsequent alteration events in addition to albitization. Tourmaline types 1-4 all have relatively high Na (median >0.8 apfu) and Mg (median ~2 apfu) contents, and low Al (median <6 apfu) contents implying substitution of Al in the Z-site by Fe^{3+}, and thus moderate to high Fe^{3+}/Fe^{2+} ratios. Importantly, type 1 tourmaline that is associated with pre-ore albitization of host rocks follows the oxydravite to povondraite trend on an AFM diagram (Henry and Guidotti 1985) and shows the clearest influence of the $Fe^{3+}Al_{-1}$ exchange in an Al - $X_{vacancy}$ + Ca vs. R + $X_{vacancy}$ – Ca + Ti diagram. All these characteristics of Type 1 tourmaline are common for tourmaline deposited from saline and relatively oxidized fluids typical of metaevaporitic environments (e.g., Henry et al. 2008; Hazarika et al. 2015); it is thus interpreted that saline fluids of an inferred metaevaporitic origin were involved in pre-ore albitization at Juomasuo. Boron isotope composition of tourmaline from Juomasuo falls under the broad range of non-marine evaporites and clastic metasediments and could reflect either of these reservoirs. By also considering the major element composition of tourmaline, these boron isotope compositions could also reflect the mixing of metaevaporitic fluids with ore-forming fluids involved in the mineralizing stages at Juomasuo.

The hydrothermal processes that affected the Juomasuo Au-Co deposit are summarized in Table 1. Widespread albitization of host rocks that preceded ore deposition was the first process that took place at Juomasuo, and based on the major element chemistry of tourmaline associated with this stage, it involved a relatively high-salinity fluid that could reflect an inferred metaevaporitic origin. The first ore-forming stage was especially Co-rich and was accompanied by chlorite (± biotite ± amphibole) alteration. Relatively reduced conditions prevailed during this stage based on the dominance of pyrrhotite. The second ore-forming stage deposited most of the Au in the deposit and is associated with abundant sericitization. Pyrite geochemistry indicates that a relatively oxidized fluid incursion was responsible for this late mineralizing stage that locally overprinted previously deposited Co-rich ore.

Table 1. Paragenetic table showing major alteration and mineralization events at Juomasuo. Table was taken from Vasilopoulos et al. (2021).

Alteration/ mineralization stage	Pre-mineralization alteration	Mineralization stage 1	Mineralization stage 2
Alteration type	Albitization	Fe-Mg metasomatism	K-metasomatism
Nature of fluid(s)	Saline fluid related to metaevaporites	Relatively reduced, metamorphic	Incursion of relatively oxidized fluid
Characteristic of mineralization stage	No mineralization	Co-rich mineralization with some Au enrichment	Au-rich mineralization with lesser Co enrichment



6.3 Article II

Mineralogical, lithogeochemical and sulfide trace element characteristics of the Hirvilavanmaa Au-only and the base metal-rich Naakenavaara orogenic gold deposits in the Central Lapland belt, northern Finland.

Mikael Vasilopoulos, Ferenc Molnár, Jukka-Pekka Ranta, Hugh O’Brien, 2023

Journal of Geochemical Exploration 244, 107132

The focus of Article II is to compare ore-forming processes in the Hirvilavanmaa Au-only and the atypical base metal-rich Naakenavaara orogenic gold deposits occurring in the vicinity (within a 5 km distance) of each other, along the same ore-controlling structures in the Central Lapland belt (CLB). In this study, we present and compare sulfide trace element characteristics from these deposits, supported by mineralogical and lithogeochemical observations in order to understand the reasons that resulted in their different metal associations. Principal component analysis was also used on lithogeochemical and pyrite trace element data to help distinguish processes and elemental associations in the deposits.

Both Hirvilavanmaa and Naakenavaara are characterized by pre-ore albitization of host rocks, something that is typical for deposits hosted along the Sirkka Shear Zone (Eilu et al. 2007). Other notable similarities in the deposits include the presence of late carbonate and chlorite alteration, and the association of metal enrichment with quartz-carbonate veins. Apart from these similarities, the two deposits have notable differences. Hirvilavanmaa is hosted in altered ultramafic metavolcanic rocks and lacks sericite and biotite alteration; pyrite dominates the sulfide mineralogy and hosts abundant native Au inclusions. Gold is the only metal significantly enriched in the Hirvilavanmaa deposit. Naakenavaara, on the other hand, is hosted in primarily metasedimentary rocks and sericite is the most prominent alteration mineral in the ore zones, with biotite also present in Cu-rich parts of the deposit. Ore mineralogy at Naakenavaara is dominated by pyrrhotite and chalcopyrite, indicating generally more reduced conditions compared to Hirvilavanmaa. Gold at Naakenavaara is locally enriched within zones of Cu and Co enrichment. Copper is the most evenly enriched metal in the deposit, with zones of significant Co enrichment being scarcer.

Pyrite from Naakenavaara has higher Co, As, Se, and Bi contents, and higher Co/Ni and Se/S ratios compared to pyrite from Hirvilavanmaa, which in turn is more enriched in Ni, Cu, Ag, Au, and Pb (Fig. 6a). Notable differences in the trace element geochemistry of pyrite support the premise that fluids with distinct composition, potentially reflecting different sources, were involved in the formation of the two deposits.

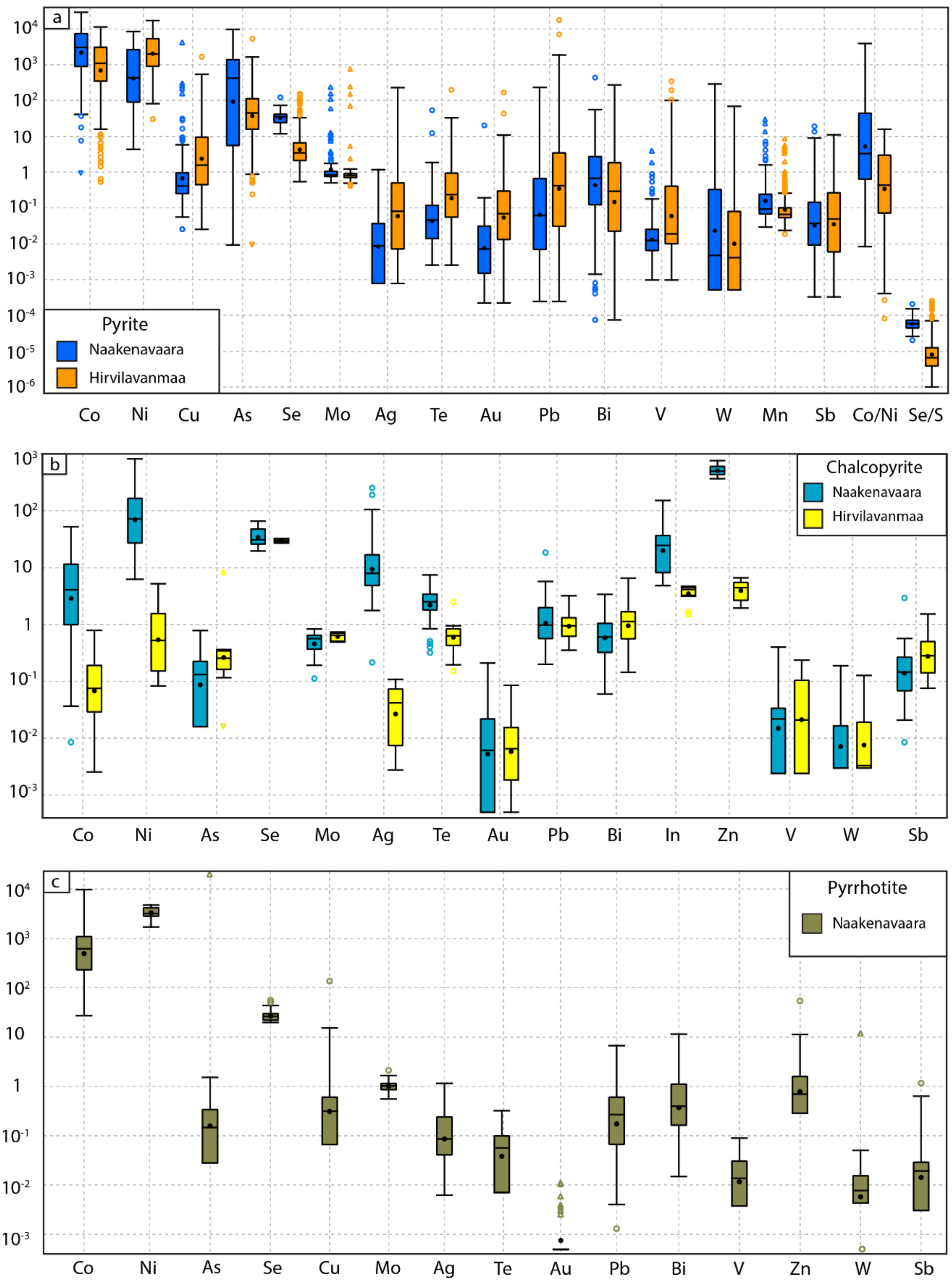


Figure 6. (a) Selected trace element boxplots with logarithmic scale for pyrite from Hirvilavanmaa (orange boxes) and Naakenavaara (blue boxes). (b) Selected trace element boxplots with logarithmic scale for chalcopyrite from Hirvilavanmaa (yellow boxes) and Naakenavaara (light blue boxes). (c) Selected trace element boxplots with logarithmic scale for pyrrhotite from Naakenavaara. Figure taken from Vasilopoulos et al. (2023).

Chalcopyrite from both deposits hosts measurable concentrations for most analyzed trace elements (Fig. 6b). Chalcopyrite from Hirvilavanmaa is generally trace element-poor. Chalcopyrite that crystallizes together with pyrite generally has low trace element concentrations as most elements preferentially incorporate into the crystal lattice of the co-existing pyrite (George et al. 2018), something that is reflected well in the trace element-poor nature of chalcopyrite from the pyrite-dominant Hirvilavanmaa deposit (Fig. 6b). At Naakenavaara, chalcopyrite dominates the Cu-rich ore, with pyrite being less abundant. As a result, chalcopyrite from Naakenavaara is significantly more enriched in trace elements, with maximum measured concentrations of 760 ppm, 819 ppm, 253 ppm, and 151 ppm for Zn, Ni, Ag, and In, respectively (Fig. 6b). The notably higher Cd/Zn ratios of chalcopyrite from Hirvilavanmaa (mean 0.69), compared to chalcopyrite from Naakenavaara (mean 0.01) indicate relatively higher crystallization temperatures for the former deposit, as Cd/Zn ratios in chalcopyrite generally increase with inferred temperature of crystallization (George et al. 2018).

Pyrrhotite from Naakenavaara hosts several trace elements in measurable concentrations but is especially enriched in Co and Ni (Fig. 6c) that can be hosted in the crystal lattice of pyrrhotite (e.g., Kresse et al. 2018). High concentrations of these two elements (up to 0.9 wt% and 0.5 wt% for Co and Ni, respectively) make pyrrhotite a notable host of Co and Ni at Naakenavaara.

Several pyrites from Hirvilavanmaa plot above the solubility line for orogenic gold deposits (Deditius et al. 2014) in a Au-As scatterplot (Fig. 7c), revealing that higher Au concentrations in analyzed pyrite represent evenly distributed Au nanoparticles. Three pyrite generations (Py_{Hirvi}-1, Py_{Hirvi}-2, and Py_{Hirvi}-3) with distinct Co/Ni ratios and other trace element characteristics are distinguished at Hirvilavanmaa (Fig. 7a). Differences in most trace element concentrations are progressive and remain relatively small between the three pyrite generations, highlighting the relatively constant composition of the ore-forming fluid in all mineralizing stages (Fig. 7d). Results of principal component analysis on pyrite trace element data from Hirvilavanmaa further support this conclusion.

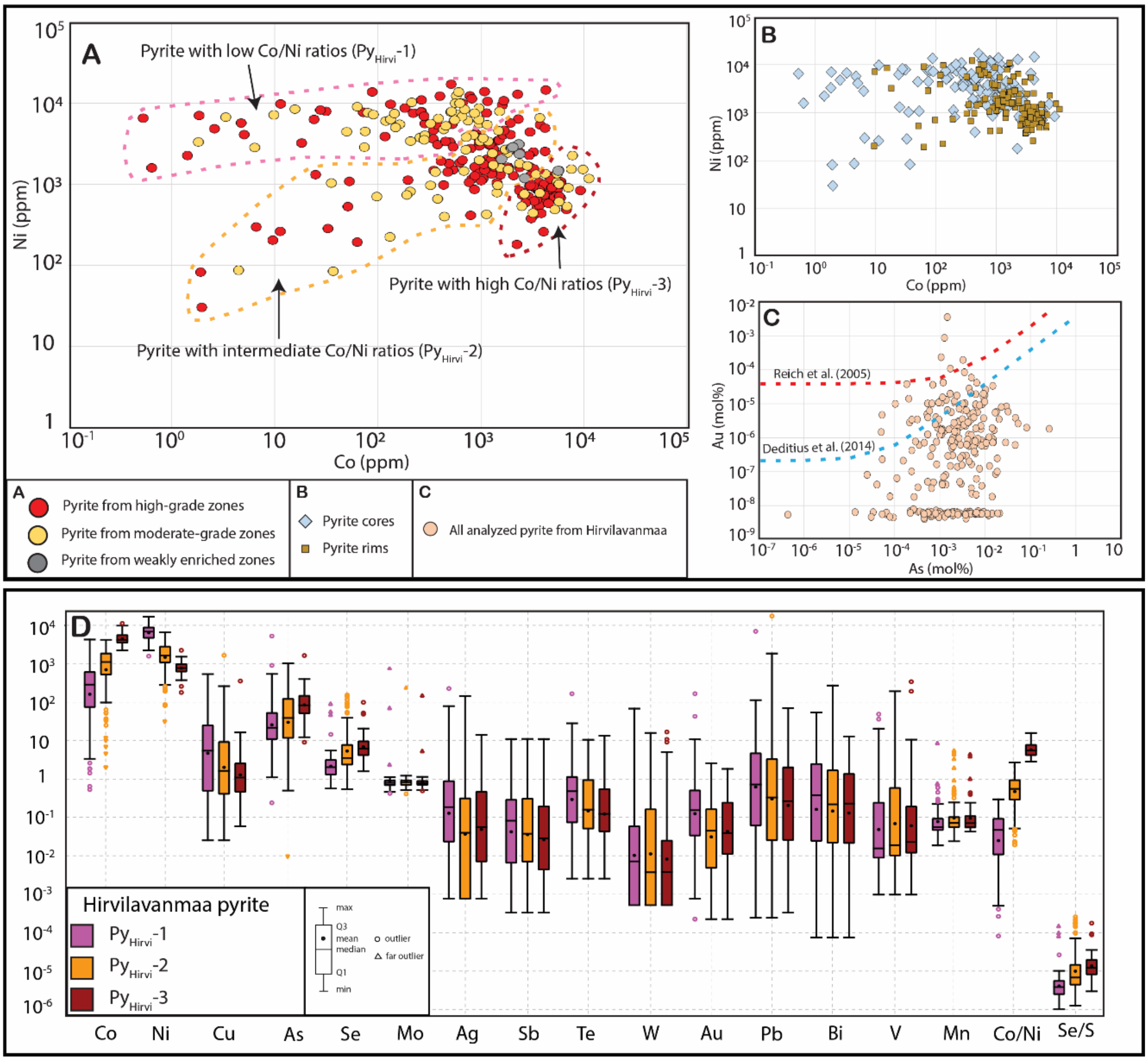


Figure 7. (A) Co-Ni plot for Hirvilavanmaa pyrite with data points classified according to degree of Au enrichment in the samples. (B) Co-Ni plot for Hirvilavanmaa pyrite with data points classified based on a core-rim distinction. (C) As-Au plot for Hirvilavanmaa pyrite with Au solubility lines from Reich et al. (2005) and Deditius et al. (2014). (D) Trace element boxplots with logarithmic scale for the different types of pyrite from Hirvilavanmaa. Figure taken from Vasilopoulos et al. (2023).

Pyrite from Naakenavaara mostly plots below the solubility line for orogenic gold deposits (Deditius et al. 2014) in a Au-As scatterplot, indicating that Au in pyrite is mostly present in solid solution in its crystal lattice (Fig. 8c). Based on paragenetic and trace element characteristics, three pyrite generations are distinguished (Fig. 8a). Pyrite (Py_{Naak}-mid) with intermediate Co/Ni ratios (mean 12.5) was deposited during the early pyrite-dominant Co-rich stage of ore formation. The subsequent Cu-rich stage deposited abundant chalcopyrite and pyrrhotite, and pyrite (Py_{Naak}-high) with high Co/Ni ratios (mean 762). Py_{Naak}-mid and Py_{Naak}-high have generally comparable trace element characteristics (Fig. 8d). A late and more restricted Au-rich stage overprinted the base metal-rich ore and deposited pyrite (Py$_{Naak}$-low) with low Co/Ni ratios (mean 0.3) and a generally distinct trace element geochemistry (Fig. 8d). The late Au-rich stage is also easily distinguished in results of principal component analysis on pyrite trace element data from Naakenavaara.

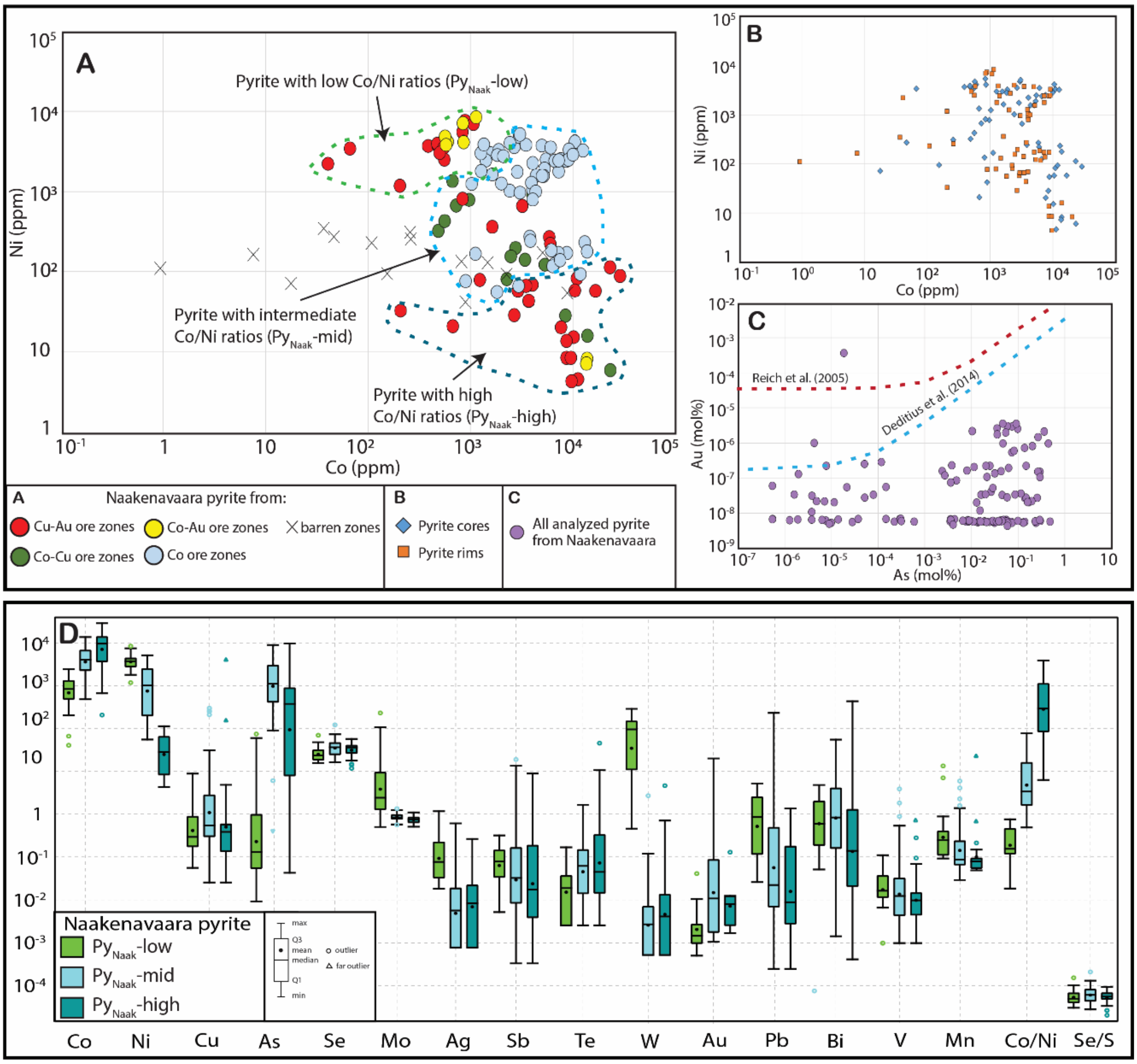


Figure 8. (A) Co-Ni plot for Naakenavaara pyrite with data points classified according to degree of Au enrichment in the samples. (B) Co-Ni plot for Naakenavaara pyrite with data points classified based on a core-rim distinction. (C) As-Au plot for Naakenavaara pyrite with Au solubility lines from Reich et al. (2005) and Deditius et al. (2014). (D) Trace element boxplots with logarithmic scale for the different types of pyrite from Naakenavaara. Figure taken from Vasilopoulos et al. (2023)

Results of PCA on whole-rock geochemical data from Hirvilavanmaa are straightforward due to the pyrite-dominated, Au-only style of mineralization and lack of host rock variability; this leads to the first principal component (PC1) representing a high degree of variability in the dataset (68.12%). At

Naakenavaara, the polymetallic and multi-stage nature of the deposit is reflected in results of PCA on whole-rock geochemical data. The complexity of element associations leads to PC1 representing just 39.85% of the variability in the dataset.

The strong structural control (Hulkki and Keinänen 2007), combined with lithogeochemical, mineralogical and sulfide trace element characteristics support an orogenic gold deposit model for the Hirvilavanmaa deposit. The As-poor character of the deposit, combined with low As, and high Co and Ni concentrations in pyrite suggest a mafic metavolcanic rock source for ore-forming components at Hirvilavanmaa.

At Naakenavaara, an early base metal-rich mineralization was locally overprinted by a late and more restricted Au-rich event. Based on the trace element characteristics of Py_{Naak}-low deposited during this late mineralizing event, this Au-rich stage can be attributed to an orogenic Au event.

6.4 Article III

U-Pb geochronology, tourmaline geochemistry, and stable (B, S) isotope constraints from the Hirvilavanmaa Au-only and the polymetallic Naakenavaaara orogenic gold deposits, Central Lapland belt, northern Finland

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The focus of Article III is on constraining the timing of ore deposition in the Hirvilavanmaa and Naakenavaara deposits and on gathering more information regarding mineralizing conditions and sources of ore-forming components. In this study, we used samples with well-established mineralogical-petrographical and geochemical characteristics and present precise U-Pb ages from hydrothermal xenotime and monazite. We also present sulfur isotope data from sulfides and crystal chemical and boron isotope data from tourmaline.

At Naakenavaara, hydrothermal xenotime hosted in a quartz-carbonate vein from a Co-only ore zone provided an age of 1816 ± 10 Ma, and it marks the beginning of ore deposition that started as an early Co-rich mineralizing stage at Naakenavaara. The base metal-rich mineralizing event that started as Co-rich subsequently evolved into the main Cu-rich stage of ore deposition (Vasilopoulos et al. 2023). Xenotime grains that are found as inclusions in pyrrhotite associated with the Cu-rich stage provided a concordia age of 1804 ± 3 Ma that marks the age for the main Cu-rich stage. The time period constrained by these two ages corresponds to the D4 deformation stage recognized by Sayab et al. (2019) in the Central Lapland belt (CLB). Ore-related hydrothermal activity had also started at Hirvilavanmaa during the same time period based on the 1822 ± 9 Ma age from xenotime hosted in the chlorite-rich alteration halo of a quartz-carbonate vein.

Hydrothermal monazite from carbonate-rich veins associated with the late Au-rich mineralizing stage at Naakenavaara provided an age of 1752 ± 10 Ma. This age corresponds withing error to the late waning stages of the Svecofennian orogeny and to the D5 deformation in the CLB during 1.77-1.76 Ga (after Sayab et al. 2019). At Hirvilavanmaa, hydrothermal monazite from ore zones gave an age of 1785 ± 10 Ma, indicating that during the late (post 1.80 Ga) stages ofthe Svecofennian orogeny Au deposition took place in both deposits.

Tourmaline hosted by altered ultramafic metavolcanic rocks in Hirvilavanmaa and Naakenavaara has exceptionally high Cr contents compared to typical values for tourmaline from orogenic gold deposits, whereas tourmaline from metasedimentary host rocks at Naakenavaara has significantly lower Cr contents. Lithological units in both deposits underwent early albitization and elevated Na contents in all tourmaline types from both deposits reflect the Na-rich character of host rocks. Based on these observations, host rock composition played an important role in controlling the major element composition of tourmaline in both deposit, something that points to relatively low fluid/rock ratios during tourmaline deposition. Both recognized tourmaline types from Hirvilavanmaa have low Al and high Fe_{tot} + Mg values, they align close to the oxydravite to povondraite trend on an AFM diagram and show influence of the $FeAl_{-1}$ exchange. These characteristics indicate relatively oxidizing conditions during ore deposition, something that fits with the pyrite-dominant character of the deposit. The same characteristics are observed in tourmaline associated with the early Co-rich mineralizing stage at Naakenavaara. Tourmaline associated with the subsequent Cu-rich stage has higher Al contents, does not align close to the oxydravite to povondraite trend and shows less influence of the $FeAl_{-1}$ exchange; these characteristics support more reducing conditions for the pyrrhotite- and chalcopyrite-dominant Cu-rich stage of ore deposition at Naakenavaara.

Results of sulfur isotope analyses from sulfides show very different distributions for Hirvilavanmaa and Naakenavaara. Sulfides from Hirvilavanmaa have a median $\delta^{34}S$ of +1.2‰, whereas sulfides from Naakenavaara have a significantly higher median $\delta^{34}S$ of +9.9‰. The clustering of the majority of sulfur isotope data close to zero combined with results of tourmaline boron isotope data support a mafic metavolcanic rock source for the ore-forming components at Hirvilavanmaa in line with the model suggested by Vasilopoulos et al. (2023). At Naakenavaara, the heavier sulfur isotope values correspond well with sulfur reduced from seawater sulfate during the Paleoproterozoic and fit with the curve describing the variation of sulfur isotope composition in sediment-hosted orogenic deposits through time (Chang et al. 2008). Thus, a metasedimentary source of sulfur is indicated for Naakenavaara. Black schists of the Savukoski Group have pyrite with high $\delta^{34}S$ values (mostly > +10‰), confirming a plausible metasedimentary source of sulfur for Naakenavaara. The shift to slightly heavier sulfur isotope compositions in pyrite deposited during the Cu-rich stage (median +9.6‰), compared to pyrite deposited during the earlier Co-rich stage (median +8.6‰) could reflect a shift to more reducing conditions during the Cu-rich stage as was also suggested based on tourmaline major element chemistry.

7. DISCUSSION

7.1 Geochemical tools in the study of ore-forming processes

For all three studied deposits lithogeochemical data provided a basis for drill core selection and were helpful in the process of drill core logging and sample selection. Different methods of lithogeochemical data analysis proved to be powerful tools that in combination with mineralogical context provided valuable information about ore-forming processes in the deposits. Lithogeochemical data were utilized most effectively in the study of the Juomasuo deposit, due to the availability of an extensive whole-rock geochemical dataset provided by Dragon Mining Ltd. (former owners of the Juomasuo property) for the purposes of this work.

The atypical orogenic gold deposits in the Kuusamo belt are characterized by pervasive albitization of host rocks that is followed by subsequent superimposing alteration related to ore-forming events (Vanhanen 2001). Albitization of host rocks, typically preceding deposition of metals, is also present in deposits hosted along the Sirkka Shear Zone in CLB (Eilu et al. 2007). The intensely altered nature of host rocks in deposits from these two greenstone belts make it in many cases challenging to determine their protoliths. Due to this factor, previous workers adopted a primarily descriptive classification of host rocks based on the dominant alteration mineralogy in the Juomasuo deposit (Pankka et al. 1991; Vanhanen 2001). Based on detailed drill core logging and locally preserved primary textures, it was determined that the host lithology comprises metasedimentary and meta-igneous rocks. The use of immobile elements for discriminating altered igneous rocks has been proposed already in the 1970s (e.g., Winchester and Floyd 1977); the Zr/TiO_2 vs. Nb/Y diagram of Pearce (1996) is widely accepted as a proxy to the TAS diagram (Le Bas et al. 1986) for classifying altered meta-igneous rocks and it proved to be very effective in classifying the heavily altered meta-igneous units at Juomasuo and in studying the relationship of protolith composition with Au and Co enrichment. The effectiveness of immobile element ratios in discriminating heavily altered host rocks at Juomasuo prove that this method could be utilized to classify host rocks even in deposits that have undergone intense multi-stage alteration.

The recognition of the different host rock types at Juomasuo had also further implications as it allowed for the application of mass-transfer calculations (Gresens 1967; Grant 1986, 1993, 2005) to the different host rock types. The pervasive alteration of host rocks made it impossible to find entirely unaltered samples at Juomasuo, but it has been shown that valuable information can be obtained from mass-transfer calculations even if the least-altered samples have still been affected by hydrothermal alteration (e.g., Molnár et al. 2016a). Results of mass-transfer calculations confirm that albitization was the first alteration event at Juomasuo, and together with petrographic observations from this study and from the study of Vanhanen (2001) that also indicate albitization predates subsequent ore-related alteration they help to confidently establish the relative timing of albitization at Juomasuo.

MER diagrams were used to identify the effects of hydrothermal alteration on each host rock type at Juomasuo and they proved to be valuable in establishing the association of Co and Au enrichment with different stages of hydrothermal activity. Thus, the research at Juomasuo proved that MER diagrams can be a powerful tool in the study of hydrothermal processes of deposits with complex multi-stage formation history.

Principal component analysis (PCA; Howarth and Sinding-Larsen 1983) has been used for exploratory data analysis of lithogeochemical and pyrite trace element data in a multitude of geochemical studies to identify and bring out multi-element associations, characterize mineral systems and to explain geological and geochemical processes in various ore deposit types (e.g., Harris et al. 1997; Grunsky 2010; Cheng et al. 2011; Wang et al. 2013; Zuo 2014; Grunsky et al. 2014; Chen et al. 2017; Chen et al. 2019; Dmitrijeva et al. 2019; Mishra et al. 2021). Despite its proven potential to assist in the interpretation of geochemical data, geochemical studies of Finnish ore deposits utilizing PCA for data analysis are limited. In this study PCA was utilized as a data analysis method in all three research targets. PCA applied to lithogeochemical data from all three research targets helped to uncover element associations and in the atypical deposits it provided further support to the connection of base metal and gold enrichments with different stages of hydrothermal processes. PCA applied to pyrite trace element data proved efficient in visualizing whether all pyrite generations in a deposit are related to the same mineralizing events. Results of this study indicate that PCA can be a valuable data analysis tool that could be utilized more in geochemical studies concentrating on orogenic gold deposits from Finland; PCA can be especially valuable in uncovering the complex hydrothermal processes involved in the formation of orogenic gold deposits with atypical metal associations.

It is well-documented that pyrite acts as a sink for numerous trace elements (e.g., Huston et al. 1995; Barker et al. 2009; Large et al. 2009). This was confirmed by this study, as pyrite from all research targets was significantly enriched in a plethora of trace elements. Importantly, Co and Ni can be involved in isovalent substitutions with Fe^{2+} in pyrite, whereas Se and As have the ability to serve as anions and partially replace S in the pyrite lattice (George et al. 2018). These four elements generally remain in the pyrite lattice even during later recrystallization events (Large et al. 2009). The Co/Ni ratio in pyrite and the concentrations of Co, Ni, As, Se and other trace elements have been used to distinguish multiple pyrite generations and mineralizing stages in ore deposits (e.g., Belousov et al. 2016; Raič et al. 2022), to classify ore deposits (e.g., Belousov et al. 2016; Gregory et al. 2019) and to study ore forming-processes (e.g., Reich et al. 2013; Keith et al. 2018). In this study pyrite trace element geochemistry played a central role and it was successfully used for all of the above-mentioned purposes. Especially the Co/Ni ratio proved to be a powerful tool in discriminating between different pyrite generations in all three studied deposits. In the atypical Juomasuo and Naakenavaara deposits, contrasting Co/Ni ratios combined with differences in the concentration of other trace elements helped to distinguish pyrite generations associated with the base metal-rich and late Au-rich stages of ore formation, respectively. Low Co/Ni ratios of pyrite deposited during the Au-rich stage at Naakenavaara fit with an orogenic Au model for this stage; similarly low Co/Ni ratios also provided further confirmation for an orogenic Au classification of the Hirvilavanmaa deposit. In addition to Co/Ni ratios, other trace element concentrations also provided valuable information. Concentrations of Au, As, Se, Te, As, Co, Ni, and W all proved useful in determining different characteristics in the studied deposits, such as the presence of Au in a free form or solid solution in the nanoscale, and the source of mineralizing fluids. Notably, the generally similar trace element geochemistry of the three pyrite generations at Hirvilavanmaa helped to establish that the fluid composition remained relatively constant through all stages of ore formation. Results of this study confirm the usefulness of pyrite trace element geochemistry in the study of hydrothermal ore deposits.

Pyrite geochemistry proved especially instrumental in determining sources of ore-forming components in the Hirvilavanmaa and Naakenavaara deposits. The high Co and Ni contents, and the characteristically low As contents in hydrothermal pyrite and in the deposit as a whole support a mafic metavolcanic source for ore-forming components at Hirvilavanmaa. This model is further supported by the generally near-zero distribution of sulfur isotope data from sulfides that fits with a magmatic signature (e.g., Ohmoto 1986), but can also indicate leaching of sulfur from igneous rocks (e.g., Li et al. 2018); boron isotope data from tourmaline also indicate a mafic metavolcanic rock source. At Naakenavaara, sulfur isotope data from pyrite and other sulfides (median +9.9‰) support a metasedimentary source of sulfur for all mineralizing stages. Black schists of the Savukoski group have pyrite with high $\delta^{34}S$ values (mostly > +10‰; Hanski and Huhma 2005), making them a plausible source of sulfur for Naakenavaara. It has been shown that large amounts of Au were liberated from mafic metavolcanic rocks of the Kittilä suite during metamorphism (Niiranen et al. 2015; Patten et al. 2020; Patten et al. 2023), making them a potential source for the Au at Hirvilavanmaa. Patten et al. (2023) also showed that no significant amounts of base metals were mobilized from mafic metavolcanic rocks in the CLB during metamorphic devolatilization, whereas significant amounts of Cu were mobilized from metasedimentary rocks; mobilization of Au from metasedimentary rocks was much less pronounced compared to the mafic metavolcanic rocks. Based on their results, the cited authors proposed that metamorphic devolatilization of Kittilä suite rocks produced fluids enriched in Au and poor in base metals, due to the large proportion of metavolcanic rocks, leading to formation of classic Au-only orogenic mineralization; fluids derived from Savukoski Group rocks are significantly more enriched in Cu and relatively poor in Au, due to the large proportion of metasedimentary rocks, thus leading to formation of atypical orogenic Au deposits. Results from this study fit well with the proposed model of Patten et al. (2023) and give further support to the premise that Au-only and atypical orogenic gold deposits in the CLB have different sources of ore-forming components.

This study proved that valuable information can be extracted from the trace element geochemistry of pyrrhotite and chalcopyrite, two sulfide minerals that are commonly neglected compared to pyrite in sulfide trace element studies. Pyrrhotite from Juomasuo and Naakenavaara was enriched in several trace elements, but especially in Co and Ni that can be hosted in its crystal lattice (Kresse et al. 2018). The relatively high contents of these two elements indicate that pyrrhotite is a notable host of Co and Ni in atypical base metal-rich deposits that have a pyrrhotite-dominant sulfide mineralogy. Chalcopyrite is thought to be poorly enriched in trace elements compared to pyrite and pyrrhotite (Cook et al. 2009, 2011; George et al. 2018), but it can host numerous trace element in measurable concentrations that can be significant in some cases (George et al. 2018). Chalcopyrite from all three deposits has multiple trace elements in measurable concentrations, with chalcopyrite from the atypical Juomasuo and Naakenavaara deposits being more enriched in trace elements. The Cd/Zn ratio of chalcopyrite from Hirvilavanmaa and Naakenavaara helped to establish that formation temperatures were generally higher for the former deposit. Moreover, it was shown that chalcopyrite from Naakenavaara is not particularly enriched in elements such as Se and Hg, that could cause problems during the processing of chalcopyrite-dominant ore (George et al. 2018).

Tourmaline is very stable after crystallization and its refractory nature under various geological conditions makes it suitable for evaluating the local chemical environment during tourmaline formation (van Hinsberg et al. 2011; Molnár et al. 2016b; Ranta et al. 2017; Dutrow and Henry 2018). Crystal chemistry of tourmaline associated with pre-ore albitization at Juomasuo fits well with that of tourmaline deposited from saline and relatively oxidized fluids typical of metaevaporitic environments. Evaporites have not been yet discovered in KB despite several indications (e.g., Vanhanen 2001). However, metaevaporites have been discovered in the Peräpohja (Tapio et al. 2021) and Central Lapland (Haverinen 2020) belts that share stratigraphical and deformational characteristics with KB (Köykkä et al. 2019). Results of this study suggest that saline fluids of an inferred evaporitic origin could be involved in the formation history of the atypical Au-Co deposits in the Kuusamo belt. Major element composition of tourmaline from Hirvilavanmaa and Naakenavaara was strongly influenced by host rock composition indicating relatively low fluid/rock ratios. Tourmaline compositions from these deposits also reflect redox conditions during tourmaline deposition. It should be noted that there can be uncertainties when interpreting compositional data from tourmaline; in hydrothermal ore deposits, tourmaline composition is controlled by several factors including host rock composition, pressure and temperature conditions, fluid/rock ratios, and fluid chemistry (e.g., Henry and Dutrow 1996). In this study, these uncertainties have been reduced by interpreting tourmaline compositional data in combination with other geochemical and mineralogical information. The involvement of a saline fluid in albitization of the Juomasuo deposit proposed in this study is supported by results of fluid inclusion microthermometry by Vasilopoulos (2015), who found primary high-salinity (28-29 wt% NaCleq) carbonic-aqueous inclusions in albite from Juomasuo. Interpretations from tourmaline chemistry regarding redox conditions in the Hirvilavanmaa and Naakenavaara deposits, on the other hand, fit with mineralogical observations. Finally, boron isotope data from tourmaline in all three deposits are also considered in combination with other geochemical methods when interpreting sources of ore-forming components in the studied deposits.

7.2 Temporal constraints on orogenic gold formation in Central Lapland belt

The ages of ore deposition at Naakenavaara and Hirvilavanmaa were constrained by results of *in situ* U-Pb dating of texturally constrained hydrothermal xenotime and monazite. At Naakenavaara, concordant xenotime found within quartz-carbonate veins associated with the early Co-rich stage provided an age of 1816 ± 10 Ma, which essentially marks the beginning of ore deposition in the deposit. Xenotime grains found as inclusions in pyrrhotite within quartz-carbonate veins associated with the main Cu-rich stage of ore deposition at Naakenavaara provided an age of 1804 ± 3 Ma. The time period constrained by these two ages at Naakenavaara corresponds to a regional deformation event, which correlates with an oblique collision of the Volgo-Sarmatia and Fennoscandia protocontinents at 1.82-1.80 Ga (Bogdanova et a. 2015; Sayab et al. 2021) and is part of the D4 deformation stage in CLB as established by Sayab et al. (2019). During the same time vein opening and pyrite deposition had also started at Hirvilavanmaa, based on the 1822 ± 9 Ma age of xenotime hosted in a pyrite- and chlorite-rich alteration halo of a quartz-carbonate vein. Similar (~1820 Ma) ages have been recorded in monazite from the Saattopora deposit (Molnár et al. 2019), showing that this deformation event was especially important for ore deposition of deposits along the SiSZ. The same deformation event also caused re-opening of previously formed veins without gold deposition in the Iso-Kuotko deposit hosted along the KiSZ (Molnár et al. 2018); this indicates that this time period between 1.82-1.80 Ga was probably less important for ore formation in the KiSZ.

A second period of ore formation in the late (post 1.80 Ga) stages of the Svecofennian orogeny is marked by U-Pb ages of monazite from both deposits. The 1752 ± 10 Ma age from Naakenavaara marks the late episode of Au deposition and corresponds within error to the waning stages of the Svecofennian orogeny and to D5 as established by Sayab et al. (2019) at ca. 1.77-1.76 Ga. The 1785 ± 10 Ma age from Hirvilavanmaa could fit within error with an orogenic extension stage at a. 1.80-1.77 Ga before D5 (Sayab et al. 2019), or with the late 1.77-1.76 Ga deformation stage that affected Au deposition at Naakenavaara. Similar (post 1.80 Ga) ages of ore deposition have been reported in the Saattopora (Mänttäri 1995; Molnár et al. 2017a) and Levijärvi-Loukinen (Molnár et al. 2017a) deposits along the SiSZ, and the Iso-kuotko deposit along the KiSZ (Molnár et al. 2018), proving that these late deformation stages were important in terms of metallogeny for deposits along both the SiSZ and the KiSZ in the CLB.

The Central Lapland, Kuusamo and Peräpohja belts of northern Finland have a similar stratigraphy and a largely shared deformational history between 1.93-1.76 Ga (Köykkä et al. 2019; Lahtinen and Köykkä 2020). The 1.82-1.80 Ga (D4) deformation that resulted in gold and base metal mineralization in the CLB was a shield-scale event (Sayab et al. 2021) and it seems that it was also an important stage of ore deposition in the KB. According to geochronological studies by Mänttäri (1995) and Pohjolainen et al. (2017), an episode of fluid flow resulting in gold mineralization took place in the Hangaslampi deposit at ~1.83-1.81 Ga, whereas the former author also provided a ~1.82 Ga $^{207}Pb/^{206}Pb$ age from a pyrrhotite from the Meurastuksenaho deposit. As discussed previously, a second significant period of ore formation in the CLB was during the late (post 1.80 Ga) stages of the Svecofennian orogeny. Geochronological studies by Molnár et al. (2016c, 2017b) showed that gold deposition took place between 1.78-1.75 Ga at the Rompas and Palokas occurrences in the PB. Results from this work combined with results of the previously cited authors, indicate that continental-scale deformation events (at c. 1.82-180 Ga and post 1.80 Ga, respectively) that took place late in the history of the Svecofennian orogeny were metallogenically important for the three major greenstone belts of northern Finland.

The U-Pb study on Hirvilavanmaa and Naakenavaara used samples that had been previously well-characterized in terms of their sulfide trace element and mineralogical characteristics; especially pyrite trace element geochemistry helped in sample selection and in interpretation of results. It is, thus, proved that a detailed sulfide trace element study can provide a valuable basis for constraining and selecting samples, and interpreting results of *in situ* geochronological studies of hydrothermal deposits.

7.3 Genetic evolution of atypical orogenic gold deposits in northern Finland

One of the major results of this study is the recognition of a similar temporal evolution of ore deposition in the atypical Juomasuo and Naakenavaara deposits from the Kuusamo and Central Lapland belts, respectively. This conclusion is an important step towards better understanding of formation of atypical orogenic gold deposits in northern Finland. In both deposits, an early base metal-rich mineralization is followed by a late orogenic Au overprint. Results of pyrite trace element and sulfur isotope geochemistry from the Hangaslampi Au-Co deposit close (~1 km distance) to Juomasuo mirror closely the results of this work from the latter deposit, with two pyrite generations with highly contrasting Co/Ni ratios and other trace element characteristics associated with the Co- and Au-Co ore respectively (Vasilopoulos et al. 2019); it can be thus inferred that in the Hangaslampi Au-Co deposit mineralizing events followed a generally similar temporal evolution as in Juomasuo. An equivalent history of ore formation has been also established for the Rompas (Au-U) and Rajapalot (Au-Co) occurences in the Peräpohja belt (Molnár et al. 2017b; Ranta et al. 2021; Raič et al. 2022). Groves et al. (2003) proposed that several deposits classified as orogenic Au deposits with an atypical metal association represent the overprint of earlier base metal-rich mineralization by a late orogenic Au mineralization through reactivation of the same structures during subsequent events. Results from Juomasuo and Naakenavaara conform to this model; combined with results from the other previously mentioned studies from the Peräpohja and Kuusamo belts they establish that this model is relevant for atypical orogenic deposits from all three major greenstone belts of northern Finland. With many polymetallic deposits from northern Finland being classified as atypical orogenic Au deposits (e.g., Holma and Keinänen 2007; Holma et al. 2007; Eilu 2015) detailed studies including whole-rock and sulfide trace element geochemistry could help answer if the overprinting of orogenic Au mineralization on earlier base metal-rich mineralization is a widespread phenomenon in the Au-rich polymetallic deposits in northern Finland.

7.4 Implications for mineral exploration

New information produced in this study regarding the hydrothermal processes involved in formation of orogenic gold deposits with different metal associations in northern Finland could also be utilized in mineral exploration. Results of this study indicate that especially sulfide geochemistry and the Molar Element Ratio diagram have the biggest potential to assist in defining geochemical and alteration vectors to ore.

Molar Element Ratios (MER) have been used to create alteration indices and have been shown to be effective in creating vectors towards mineralization (Warren et al. 2007; Benavides et al. 2008). The MER diagram developed in this study based on the alteration mineralogy of the Juomasuo deposit proved to be helpful in distinguishing Co-rich samples related to the early Co-rich mineralizing stages from Au(-Co)-rich samples related to the later Au-rich stage in the deposit; importantly, barren samples also plot into a distinct part of the diagram (Fig. 4c-e). The MER diagram developed in this study could be used to create vectors towards mineralization in the Kuusamo belt and after appropriate selection of molar ratios, as to best represent the expected alteration mineralogy of the target areas, it could be also utilized for the same purpose in other metallogenically important areas.

It has been demonstrated that sulfides and other indicator minerals found in glacial sediments have the potential to be linked to primary mineralization, and several methods based on their geochemistry have been proven to be effective in exploration for various mineral deposit types (e.g., Averill 2011; McClenaghan et al. 2011; McClenaghan and Paulen 2018; Manéglia et al. 2018; Duran et al. 2019). As demonstrated in this study, the trace element geochemistry of pyrite, chalcopyrite and pyrrhotite can distinguish different mineralizing stages in classic Au-only and atypical orogenic gold deposits and discriminate between different deposit types. Thus, trace element and sulfur isotope geochemistry of sulfides found in till can be used to assist in mineral exploration by utilizing their Co/Ni ratios and other geochemical parameters for recognizing the types of mineralization present in target areas of exploration in the heavily glaciated greenstone belts of northern Finland.

8. CONCLUSIONS

Based on the results of research included in this dissertation the following conclusions can be drawn:

1. This study utilizes lithogeochemical, sulfide trace element and sulfur isotope, and tourmaline crystal chemical and boron isotope data in several geochemical research methods for investigating the hydrothermal processes involved in formation of the Juomasuo, Hirvilavanmaa and Naakenavaara deposits. The combination of several geochemical study methods proved especially important in understanding complex processes in the deposits.
2. The highly altered host rocks of the Juomasuo Au-Co deposit can be classified by utilizing drill core observations and bulk geochemical compositions on a Nb/Y-Zr/TiO_2 discrimination diagram. Recognized host rock types include ultramafic, mafic, intermediate and felsic meta-igneous rocks, and metasedimentary rocks. There is no major lithological control on metal enrichment, as both Au-Co and Co-only ore types occur in all host rock types except the ultramafic sill.
3. Widespread albitization predates the Au-Co mineralization at Juomasuo based on petrographic observations and results of mass-transfer calculations. Ore formation started with a Co-rich stage closely associated with chlorite alteration. A later Au-rich mineralizing stage that is linked to sericite alteration deposited most of the Au in the deposit.
4. Chemistry of tourmaline from Juomasuo associated with early albitization shows several characteristics common for tourmaline deposited from saline fluids typical of metaevaporitic environments. It should be noted that there have been recent discoveries of metaevaporites in the stratigraphically similar Central Lapland and Peräpohja belts.
5. The Hirvilavanmaa Au-only deposit from the Central Lapland belt can be confidently classified as a typical orogenic Au deposit based on its geochemical and mineralogical characteristics. Gold mineralization progressively developed during multiple pulses, but composition of the hydrothermal fluid remained relatively unchanged.
6. Whole-rock and pyrite trace element geochemistry indicate a mafic metavolcanic-rock source for ore-forming components at Hirvilavanmaa. The mostly near-zero values of sulfur isotopes and the boron isotope data from tourmaline also permit this conclusion.

7. In the Naakenavaara Cu-Co-Ni-Au deposit two spatially coincident but distinct mineralizing events were recognized based on pyrite trace element, mineralogical and lithogeochemical characteristics. Ore formation started with a base metal-rich mineralizing event that started as Co-rich before developing into its main Cu-rich stage. A later and more restricted orogenic Au event locally overprinted the base metal-rich ore zones.
8. Sulfur isotope composition of sulfides at Naakenavaara indicates a metasedimentary source of sulfur, with black schists of the Savukoski group being a possible source. These results indicate that metamorphic devolatilization of metasedimentary rocks led to formation of atypical orogenic mineralization in the Central Lapland belt.
9. Pyrite trace element geochemistry from studied deposits proved to be very effective in discriminating between different mineralizing stages. Especially, the Co/Ni ratio of pyrite proved to be a sensitive indicator. Differences in sulfide trace element geochemistry between the Hirvilavanmaa and Naakenavaara deposits also proved the usefulness of the method in discriminating between deposit types.
10. Tourmaline chemistry indicates relatively oxidizing conditions during tourmaline formation at Hirvilavanmaa and during the early Co-rich stage at Naakenavaara. More reducing conditions prevailed during the main Cu-rich stage of ore deposition at Naakenavaara.
11. At Naakenavaara, U-Pb ages of vein-hosted hydrothermal xenotime reveal that early base metal-rich mineralization took place during a deformation event between 1.82-1.80 Ga. U-Pb ages of hydrothermal xenotime reveal that vein opening and pyrite deposition had also started at Hirvilavanmaa during the same time period. Based on U-Pb ages of hydrothermal monazite from Au-rich ore zones, Au was deposited in both deposits at c. 1.78-176 Ga.
12. The late time period of the Svecofennian orogenesis (c. 1.82-1.76 Ga) marked by results of U-Pb dating of monazite and xenotime from the Hirvilavanmaa and Naakenavaara deposits proves to be especially important in terms of metallogeny in the CLB, and other Svecofennian greenstone belts of northern Finland with similar ages of mineralizing events recorded in various deposits.
13. The recognition of a base metal-rich mineralizing event being overprinted by orogenic Au mineralization in the atypical Juomasuo and Naakenavaara deposits can have important implications for understanding the origin of atypical base metal-rich orogenic gold deposits in northern Finland. Detailed geochemical studies in other atypical deposits could help answer if this temporal evolution of mineralizing events is a widespread occurrence in the atypical orogenic Au deposits in northern Finland.
14. The effectiveness of sulfide trace element geochemistry and of the Molar Element Ratio diagram in distinguishing between different mineralizing stages in the studied deposits highlight the

potential of both methods to be useful in creating vectors towards mineralization in mineral exploration projects.

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