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Marko Moilanen

Re-Os isotope systematics and iron oxide compositions of the mafic-ultramafic Ni-Cu-PGE deposits in eastern and northern Finland



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Cover Figure:

Photographs of massive sulphide drillcore samples from the Sakatti deposit.

#### Marko Moilanen

# Re-Os isotope systematics and iron oxide compositions of the mafic-ultramafic Ni-Cu-PGE deposits in eastern and northern Finland

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## **Re-Os isotope systematics and iron oxide compositions of the mafic-ultramafic Ni-Cu-PGE deposits in eastern and northern Finland**

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## ABSTRACT

Intrusive and extrusive rocks crystallised from primitive mantle-derived mafic-ultramafic magmas (e.g., komatiites, basalts, picrites) are important hosts for magmatic sulphide ore deposits of nickel, copper and platinum group elements (Ni-Cu-PGE). These metals together with cobalt (Co) are vital elements for modern society due to their use in electric cars, and especially in batteries, and therefore their demand has increased significantly over the last decade.

This PhD study comprises four research articles and is divided thematically into two parts. The first part focuses on the Re-Os isotope systematics of magmatic Ni-Cu-PGE deposits and their host rocks mostly from eastern and northern Finland and the second part on the trace element compositions of oxide phases in these deposits and some other reference deposits. Applying the Re-Os method to whole-rock and mineral separate samples, the following isochron ages were obtained for the studied Ni-Cu(-PGE) deposits: Re-Os isotope compositions indicate that the Ruossakero deposit is Archaean in age. The T<sub>RD</sub> model age of the Tulppio dunitic intrusion is  $2680 \pm 88$  Ma, which is regarded as a minimum age for the ultramafic body. The Tainiovaara deposit also yielded an Archean Re-Os isochron age,  $2753 \pm 47$  Ma. Similar Palaeoproterozoic Re-Os isochron ages were obtained for two deposits,  $2063 \pm 35$  Ma for Sakatti and 2058  $\pm$  93 Ma for Lomalampi, which are consistent with the age of the komatilitic-picritic volcanism in central Lapland.

Most of the chromite separates from the studied Palaeoproterozoic and Archaean deposits show nearchondritic initial Os compositions, indicating that their Os is mostly derived from a mantle source with a long-term chondritic Re-Os isotope evolution. There are also indications that contamination with radiogenic Os is not reflected in the Os isotope signatures of the chromite minerals, but in contrast, two chromite samples from the Lomalampi and Tainiovaara deposits show moderately positive initial  $\gamma$ Os values, which indicates contamination with radiogenic Os.

Sulphide and magnetite separates from the Sakatti deposit have radiogenic initial Os isotope compositions ( $\gamma$ Os between +21 and +56 at 2058 Ma), suggesting a minor to moderate degree of contamination with crustal material. In contrast to these minerals, chromite separates yielded chondritic  $\gamma$ Os values. This indicates that sulphur saturation took place after chromite crystallisation in the Sakatti ultramafic body. The Re-Os isotope systematics of some of the sulphide samples from the Sakatti, Vaara, Lomalampi deposits and sulphide-bearing sedimentary rocks from the Lomalampi area show resetting of the Re-Os isotope system at ca. 1.85–1.90 Ga, i.e., during the Svecofennian tectono-metamorphic events. The study demonstrates that Re-Os isotopes can be used for dating, determining the source of Os and signs of contamination and post-magmatic alteration processes in magmatic Ni-Cu-PGE deposits.

In-situ trace element compositions were determined for iron oxides from the Ruossakero Ni-(Cu) deposit, Tulppio dunite and related Ni-PGE mineralisation, Hietaharju, Vaara, and Tainiovaara Ni-(Cu-PGE) deposits and Lomalampi PGE-(Ni-Cu) deposit. Also, some reference samples from the Kevitsa (Finland), Pechenga (Russia) and Jinchuan (China) Ni-Cu-PGE sulphide deposits were studied. Barren komatiitic volcanic rocks from the Kovero area (Finland) were also included. Based on their major element compositions from massive sulphide samples, oxides in these samples are both magnetite and Cr-magnetite. The abundances of individual trace elements in oxide minerals differ by two to three orders of magnitude as a reflection from the composition of the silicate or sulphide melt from which oxide grains were crystallised. Magnesium is lowest in magnetites from massive sulphide samples (Hietaharju and Pechenga deposits), suggesting that low Mg could be a diagnostic feature of an iron oxide phase crystallised together with Fe-rich MSS (monosulphide solid solution) in a microenvironment that was more or less isolated from the associated Mg-rich silicate liquid. The average nickel concentration in magnetite is a function of the average Ni tenor (in 100% sulphide fraction) of the associated sulphide phase for both magmatic and postmagmatic magnetite (e.g., oxidation product of sulphides). It was also discovered that it is possible to use iron oxide compositions (e.g., high Ni, low Mg, high Ga in magnetites from massive sulphides and high Ni in high-Ni tenor deposits) in different discrimination diagrams and information on sulphide inclusions in oxide minerals (especially Ni-sulphide and/or PGE inclusions in magnetite) as an exploration tool and fingerprinting for magmatic Ni-Cu-PGE deposits. Especially in glaciated terrains in Fennoscandia, heavy mineral separates (e.g., magnetite and/or chromite) from till samples could be studied with this method.

**Keywords:** Re-Os isotopes, trace element, chromite, sulphide, iron oxide, magnetite, Ni-Cu-PGE deposit, Finland

## Re-Os isotoopit ja rautaoksidimineraalien koostumus mafis-ultramafisissa Ni-Cu-PGE esiintymissä Itä- ja Pohjois-Suomessa

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### TIIVISTELMÄ

Maapallon vaipasta peräisin oleva mafis-ultramafinen magma ja siitä syntyneet intrusiiviset ja ekstrusiiviset kivet (kuten komatiitit, pikriitit ja basaltit) ovat tärkeitä isäntäkiviä magmaattisille Ni-Cu-PGE-malmeille. Nämä malmit sisältävät nikkeliä, kuparia, kobolttia ja platinaryhmän metalleja, jotka ovat tärkeitä alkuaineita modernille, hiilineutraaliuteen pyrkivälle yhteiskunnalle. Esimerkiksi sähköautojen ja katalysaattoreiden määrän noustessa näiden metallien tarve on lisääntymässä kasvavalla vauhdilla.

Tämä väitöskirja perustuu neljään tutkimusartikkeliin ja on jaettu kahteen osaan. Ensimmäisessä osassa käsitellään Pohjois- ja Itä-Suomessa esiintyvien magmaattisten Ni-Cu-PGE-esiintymien Re-Os-isotooppikoostumuksia ja toisessa osassa näiden esiintymien rautaoksidien hivenalkuainekoostumuksia. Tulosten mukaan saatiin seuraavia Re-Os-ikämäärityksiä Ni-Cu-PGE-esiintymille: Ruossakeron Ni-(Cu)-esiintymä on iältään arkeeinen. Tulppion duniitille määritettiin  $T_{RD}$ -malli-ikä 2680 ± 88 Ma, joka on sen minimi-ikä. Tainiovaaran Ni-(Cu-PGE)-esiintymälle määritettiin Re-Os-isokrooni-ikä 2753 ± 47 Ma. Sakatin Cu-Ni-PGE-esiintymälle saatiin Re-Os-ikämääritys 2063 ± 35 Ma ja Lomalammen PGE-(Ni-Cu)-esiintymälle 2058 ± 93 Ma. Tutkittujen arkeeisten ja paleoproterotsooisten esiintymien kromiittien initiaalinen Os-isotooppikoostumus on lähellä kondriittista, joka kertoo sen, että osmium on suurelta osin peräisin vaipan lähteestä, jolla on kondriittinen Re-Os-isotooppievoluutio. Yleisesti kromiittin koostumuksen perusteella näyttää siltä, että kontaminoituminen radiogeenisellä osmiumilla ei näy kromiittien koostumuksessa, mutta kuitenkin kaksi kromiittinäytettä Lomalammen ja Tainiovaaran esiintymistä antavat kohtalaisen positiivisen initiaali  $\gamma$ Os-arvon, joka indikoi mahdollista kontaminoitumista radiogeenisellä osmiumilla.

Sulfidi- ja magnetiittiseparaatit Sakatin esiintymästä ovat radiogeenisiä initiaalisten yOs-arvojen vaihdellessa arvosta +21 arvoon +56 (2058 Ma), mikä viittaa kontaminoitumiseen kuorellisella materiaalilla. Suurin osa Sakatin esiintymästä analysoiduista kromiittiseparaateista on isotooppikoostumukseltaan kondriittisia, kun taas sulfidien yOs-arvot ovat ei-kondriittisia. Tämä voisi johtua siitä, että magman kyllästyminen sulfidisulasta tapahtui kromiitin kiteytymisen jälkeen. Jotkin Sakatin, Lomalammen ja Vaaran esiintymien sulfidinäytteiden ja Lomalammella esiintyvien mustaliuskeiden Re-Os-isotooppikoostumukset näyttävät tasapainottuneen uudelleen noin 1.85-1.90 Ga vuotta sitten svekofennisten orogeenisten tektonis-metamorfisten prosessien aikana. Tämä tutkimus osoitti, että Re-Os-isotooppeja voidaan käyttää Ni-Cu-PGE-esiintymien ikämääritysiin, osmiumin lähteen tutkimiseen ja myöskin kontaminaation ja post-magmaattisten prosessien tutkimiseen.

Väitöskirjan toisessa osassa tutkittiin rautaoksidien hivenalkuainekoostumuksia seuraavista esiintymistä: Ruossakeron Ni-(Cu)-esiintymä, Tulppion duniitti ja siihen liittyvä Ni-PGE-mineralisaatio, Hietaharjun, Vaaran ja Tainiovaaran Ni-(Cu-PGE)-esiintymät ja Lomalammen PGE-(Ni-Cu)-esiintymä. Joitakin referenssinäytteitä tutkittiin myös Kevitsan, Petsamon ja Jinchuanin Ni-Cu-PGE-esiintymistä ja Koveron alueen ei-mineralisoituneista komatiittisista kivistä. Pääalkuainekoostumuksen mukaan massiivisten sulfidinäytteiden rautaoksidit olivat magnetiittia ja Cr-magnetiittia. Tutkittujen rautaoksidien hivenalkuainekoostumus vaihteli kahdesta kolmeen kertaluokkaan, mikä kuvastaa alkuperäisten silikaattija/tai sulfidisulien koostumusta, joista nämä rautaoksidit ovat kiteytyneet. Magnetiittien Mg-pitoisuus oli alhaisin massiivisissa sulfidinäytteissä (Hietaharju ja Petsamo), mikä voi olla diagnostinen piirre rautaoksideille, jotka ovat kiteytyneet yhdessä monosulfidisen kiinteän liuoksen (MSS) kanssa tämän mikrosysteemin ollessa eristyksissä Mg-rikkaasta silikaatti sulasta. Tutkimuksissa tuli myös ilmi, että keskimääräinen magnetiitin Ni-pitoisuus on lähestulkoon suoraan verrannollinen esiintymän keskimääräiseen Ni-tenoriin (100 % sulfidiksi laskettuna). Tämä havaittiin alkuperältään magmaattisissa ja myös post-magmaattisissa magnetiiteissa, kuten sulfidien hapettumisen kautta syntyneissä magnetiiteissa. Tutkimukset osoittivat myös, että magnetiitin koostumuksesta (kuten korkea Ni-pitoisuus, alhainen Mgpitoisuus, korkea Ga-pitoisuus magnetiiteissa, jotka ovat peräisin massiivisista sulfideista ja korkea Nipitoisuus magnetiiteissa, jotka ovat korkean Ni-tenorin omaavista esiintymistä) johdettuja diskriminaatiodiagrammeja ja sulfidisulkeumien esiintymistä magnetiiteissa (erityisesti Ni-sulfidit ja/tai PGE-sulkeumat) voidaan käyttää Ni-Cu-PGE malmien etsinnässä. Erityisesti tätä menetelmää voisi hyödyntää malminetsinnässä Fennoskandiassa ja muilla jäätiköityneillä alueilla; moreenin raskasmineraalifraktioista erotetun magnetiitin hivenalkuainekoostumuksen perusteella voitaisiin arvioida, onko magnetiitti peräisin Ni-Cu-PGE esiintymästä.

Asiasanat: Re-Os isotoopit, hivenalkuaine, kromiitti, sulfidi, rautaoksidi, magnetiitti, Ni-Cu-PGE-esiintymä, Suomi

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Kiiminki, August 2022,

Marko Moilanen

#### **ORIGINAL PUBLICATIONS \***

- Paper I: Törmänen, T., Konnunaho, J.P., Hanski, E., Moilanen, M., Heikura, P., 2016. The Paleoproterozoic komatiite-hosted PGE mineralization at Lomalampi, Central Lapland Greenstone Belt, northern Finland. *Mineralium Deposita* 51, 411–430.
- Paper II: Moilanen, M., Hanski, E., Konnunaho, J., Yang, S-H., Törmänen, T., Li, C., Zhou, LM., 2019. Re-Os isotope geochemistry of komatiite-hosted Ni-Cu-PGE deposits in Finland. Ore Geology Reviews 105, 102–122.
- Paper III: Moilanen, M., Hanski, E., Yang, S-H., 2021. Re-Os isotope geochemistry of the Palaeoproterozoic Sakatti Cu-Ni-PGE sulphide deposit in northern Finland. Ore Geology Reviews, 132.
- Paper IV: Moilanen, M., Hanski, E., Konnunaho, J., Törmänen, T., Yang, S-H., Lahaye, Y., O'Brien, H., Illikainen, J., 2020. Composition of iron oxides in Archean and Paleoproterozoic mafic-ultramafic hosted Ni-Cu-PGE deposits in northern Fennoscandia: application to mineral exploration. *Mineralium Deposita* 55, 1515– 1534.

\* Note that the original publications are not included in the electronical version of the PhD thesis. The original articles were reprinted in the paper version of the thesis and some figures were used in the paper and electric versions with the permissions of Elsevier (papers II and III) and Springer (paper I) publishing companies. Paper IV is an open access article.

Marko Moilanen is the main author of papers II, III and IV, with the co-authors participating by writing, commenting, and providing important corrections and ideas. Marko Moilanen is the fourth co-author of paper I, which is the result of a follow-up study of Moilanen's MSc project. The scope of the research of papers II and IV were planned together with Marko Moilanen, Eero Hanski, Jukka Konnunaho, Shenghong Yang, and Tuomo Törmänen. The Geological Survey of Finland (GTK) provided some of the thin section samples for the studies of papers I, II and IV. The scope of the research and sampling for the Re-Os study of paper III were planned by Marko Moilanen, Eero Hanski and Shenghong Yang together with Jukka Jokela, Janne Siikaluoma and Outi Ahvenjärvi from the mining company (AA Sakatti Mining Oy). Marko Moilanen carried out most of the sample preparation for papers II and III and half of the sulphur isotope samples for paper I. Data processing and modelling included in papers II, III and IV were mostly done by Marko Moilanen. Re-Os analyses were performed by Chao Li and Liming Zhou for paper II and Igor and Valentina Puchtel for paper III. EPMA analyses for paper IV were mostly conducted by Marko Moilanen and some by Jussi Illikainen together with Marko Moilanen and all the LA-ICP-MS analyses were carried out by Marko Moilanen with the help of Yann Lahaye and Hugh O'Brien. All the co-authors and reviewers have helped in writing and correcting of the four research articles.

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#### **1 INTRODUCTION**

Nickel (Ni), copper (Cu), cobalt (Co), and platinum group elements (PGE) are crucial metals for modern society. For example, the growing demand of clean energy technologies, such as batteries for electric cars, technologies for solar, wind, and geothermal power applications, and energy storage solutions, require these metals from primary and recycled sources. These energy technologies are important when investing in the transformation to a more low-carbon economy, which helps to control the climate change. Magmatic Ni-Cu-Co-PGE sulphide deposits host all of the above-mentioned important metals, and therefore research and exploration of these deposits is very important now and in the future.

This research was part of the Mineral Systems and Mineral Prospectivity Mapping in Finnish Lapland project (MINSYSPRO) funded by the Academy of Finland. The overall objective of the project was to support the development of cost-effective, environmentally friendly exploration methods by implementation of new knowledge from research on orogenic gold and magmatic sulphide mineral systems into computer-based mineral prospectivity mapping. This study belonged to the subproject (project #281859) concerning magmatic mineral systems, in which new data were gathered from several Ni-Cu sulphide deposits occurring in different greenstone belts in Finland.

The dissertation is divided thematically into two parts: the first part deals with the application of the Re-Os isotope system to magmatic Ni-Cu-PGE sulphide deposits and the second part concerns trace element compositions of iron oxides from these deposits.

Rhenium (Re) and Osmium (Os) are both concentrated in varying amounts in magmatic sulphide liquid, sulphide minerals, oxide and mafic silicate minerals and therefore, the Re-Os isotopic system has been used extensively for studying sulphide ore genesis. The Re-Os isotopic system can be utilised for dating sulphides, oxides and silicates and for determining the source of Os in magmatic sulphide ore deposits and the degree of potential crustal contamination of magmas.

There are several studies in which the Re-Os system has previously been applied to maficultramafic rocks and related ore deposits in Finland. These studied layered intrusions include the Kevitsa intrusion (Hanski et al., 1997), the Koitelainen and Akanvaara intrusions (Hanski et al., 2001a), and the Kemi intrusion (Yang et al., 2016). Gangopadhyay et al. (2006) and Puchtel et al. (2020) have published Re-Os isotope data for 2.06 Ga komatiites from the Central Lapland greenstone belt (currently called the Central Lapland Belt). The Värriö ultramafic complex in eastern Lapland was investigated with the Re-Os isotopic system (Heller, 2020). In southern Finland, Svecofennian Ni-Cu deposits were studied by Lähteenmäki et al. (2007), obtaining a Re-Os isochron age of  $1993 \pm 29$  Ma for these deposits.

Re-Os isotopes have also been utilised in studies of ophiolitic rocks in Finland (Walker et al., 1996; Tsuru et al., 2000). Walker et al. (1996) showed that chromite, gersdorffite and laurite separates from the upper mantle rocks of the 1.97 Ga Outokumpu ophiolite have a broadly chondritic composition. Tsuru et al. (2000) in turn demonstrated that the ca. 1.95 Ga Jormua ophiolite complex displays large Os isotopic heterogeneities. They concluded that the variation may indicate that the Jormua mantle rocks were derived both from MORB-type (chondritic) mantle and subcontinental lithospheric mantle sources. Peltonen and Brügmann (2006) measured Re-Os isotope compositions of mantle xenoliths from kimberlites from the Kaavi-Kuopio area and showed that the subcontinental lithospheric mantle (SCLM) at the Karelian Craton margin (in the Fennoscandian Shield) can be divided into three distinct layers (called A, B and C), and that layer A is absent in the core of the craton, and therefore its origin is related to underthrusting of a Proterozoic arc complex beneath the craton margin crust during continental collision about 1.9 Ga ago.

Since the advent of precise in-situ analytical methods, particularly laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), trace element compositions of iron oxides have drawn much attention during the last decade. This development allows to obtain information on iron oxide compositional variation in magmatic Ni-Cu-PGE deposits formed from different parental magmas or deposits that re-equilibrated under different post-magmatic conditions. It also provides an opportunity to test whether iron oxide compositions can be used as an exploration tool for new magmatic Ni-Cu-PGE deposits. Especially in glaciated terrains in Fennoscandia, heavy mineral separates (e.g., magnetite) extracted from till samples could be studied with this new method.

## 2 CLASSIFICATION AND GENESIS OF MAGMATIC Ni-Cu-PGE SULPHIDE DEPOSITS

Mafic-ultramafic intrusive and extrusive rocks are important host rocks for magmatic Ni-Cu-Co-PGE sulphide deposits. The parental magmas to the igneous bodies containing these deposits could be mafic to ultramafic in composition, such as picrite, basalt or komatiite, and the deposits can be classified according to their parental magma composition and Ni/Cu ratio (e.g., Naldrett, 2004; Barnes and Lightfoot, 2005). Also, geological association can be used as the basis for classification (e.g., Barnes and Lightfoot, 2005), including, for example, astroblemes (Sudbury), rift-related feeders to continental flood basalts (Noril'sk-Talnak, Jinchuan), province boundary feeders (Voisey's Bay), rift environments with komatiitic lava flows and intrusions (Kambalda, Thompson, Alexo, Texmont), or rift environments with picritic lava flows and intrusions (Pechenga), and orogenic activity-related intrusions (Kotalahti and Vammala belts). Also, the primary Ni-Cu-PGE mineralisation type (type I massive sulphide deposits, type II disseminated sulphide deposits and type III reef-type deposits, and type IV-V post-magmatically modified deposits) can be used for classification (e.g., Arndt et al., 2005; Lesher and Keays, 2002). Still one way to classify magmatic sulphide deposits is that based on the relative abundances of chalcophile elements (Lu et al., 2019), with the classes being : I) Ni-Cu-Co-PGE deposits that have relatively smooth mantle-normalised chalcophile metal patterns (e.g., Kambalda-Mt. Keith-Perseverance komatiites, Raglan komatiites, Duluth, Norilsk-Talnakh, Sudbury, Thompson), II) Ni-Cu-Co-PGE deposits that are depleted in PGE relative to base metals (e.g., Pechenga, Jinchuan, Voisey's Bay), and III) PGE-Ni-Cu-Co deposits that are enriched in PGE compared to base metals (e.g., Bushveld Complex, Great Dyke, Stillwater).

The formation history of magmatic Ni-Cu-PGE sulphide deposits can be divided into several stages (e.g., Barnes and Lightfoot, 2005; Naldrett, 2004; Naldrett, 2010). They are summarised below and more detailed consideration of some aspects that are relevant to this study are dealt with in Chapter 3.

1) Partial melting of the mantle. Mantle-derived primitive magmas (e.g., komatiites) are generated by a high degree of mantle melting (e.g., Arndt et al., 2005; Naldrett, 2004; Naldrett, 2010), which is needed to release metals from mantle minerals (e.g., olivine, pyroxenes, spinel, base metal sulphides) to melt. The Ni content of the melt is mostly controlled by melting of olivine, with Ni increasing progressively with the degree of partial melting, whereas the concentrations of other chalcophile elements, particularly PGE, are influenced by melting of mantle base metal sulphides. It has generally been concluded (e.g., Barnes et al., 1985; Keays, 1995; Mungall and Naldrett, 2008; Naldrett, 2010; Fonseca et al., 2011; 2012, Kiseeva et al., 2017) that it requires 18–25% partial melting for all the base metal sulphides to become dissolved, releasing their whole chalcophile element budget to the melt. Consequently, the melts produced by moderate degrees of melting are highest in PGE and Cu (e.g., Barnes and Lightfoot, 2005; Naldrett, 2004; Naldrett, 2010; Mungall and Naldrett, 2008).

2) Magma transportation to the crust. The solubility of sulphur in silicate melts is dependent on pressure, becoming higher with decreasing pressures, and therefore when a mantle-derived magma rises to crustal levels, it is usually sulphur undersaturated (Mavrogenes and O'Neill, 1999; Smythe et al., 2017). Before the final emplacement of the magma to the crust, fractionation of olivine

and/or sulphides should not be too extensive, because it will result in depletion of Ni and other chalcophile elements in the magma.

3) Sulphide saturation. An originally S-undersaturated magma can reach sulphide saturation by several mechanisms, such as fractionation crystallisation, a temperature decrease, pressure increase, oxygen fugacity (fO<sub>2</sub>) increase, sulphur fugacity (fS<sub>2</sub>) decrease, magma mixing, change in magma composition by adding volatiles or adding S, SiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O from country rocks to magma, (e.g., Arndt et al., 2005; Barnes and Lightfoot, 2005; Ripley and Li, 2003, 2013; Naldrett, 2004; Mungall and Naldrett, 2008). The most effective mechanism is introduction of external sulphur to magma from sulphur-bearing crustal material (e.g., Mavrogenes and O'Neill, 1999; Lightfoot and Keays, 2005; Keays and Lightfoot, 2010). As a magma reaches a crustal level, it may interact with sulphur-bearing sedimentary rocks, such as black shale strata or anhydrite beds, assimilating sulphur either by bulk or partial melting of the country rocks or devolatilisation (Lesher and Burnham, 2001).

4) Collection of chalcophile elements. Attainment of sulphur saturation leads to the formation of immiscible sulphide liquid droplets, which collect chalcophile metals from the associated silicate melt due to their high sulphide melt/silicate melt partition coefficients (Barnes and Lightfoot, 2005, and references therein). However, the metal concentrations of the sulphide phase are not only dependent on these coefficients and the metal concentrations in the silicate melt but also on the R factor. The R factor (Campbell and Naldrett, 1979) expresses the ratio of the mass of silicate magma to the mass of sulphide, i.e., the relative amount of the silicate liquid with which the sulphide liquid equilibrated. High R factors are typical of the deposits that are formed from a huge amount of magma, allowing the formation of PGE-enriched deposits, such as PGE reefs in large, layered intrusions. Low-R-factor deposits are formed from a lesser amount of magma in highly dynamic magma systems and are base metal-dominated sulphide deposits, such as Ni-Cu sulphide deposits in komatiitic lava flows and conduits and/or sills (e.g., Naldrett, 2004; Barnes and Lightfoot, 2005; Barnes and Maier, 1999).

5) Formation of a magmatic sulphide deposit. The magmatic sulphide deposits are formed by mechanical segregation of immiscible sulphide droplets from the associated silicate melt, concentrating them to an economically feasible level in structural traps in lava flows, subvolcanic sills or intrusion for base metal-dominated deposits, and on a cumulate pile of large magma chambers to form PGE-rich reefs (e.g., Barnes and Lightfoot, 2005; Naldrett, 2004, and references therein).

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6) Postmagmatic modification and enrichment of metals. After their emplacement, many magmatic Ni-Cu-PGE deposits have been deformed and suffered from various alteration processes including serpentinisation, chloritisation, carbonatisation, oxidation, and desulphurisation. Particularly oxidation and desulphurisation may lead to the formation of Ni-rich secondary sulphides, such as millerite and violarite, upgrading of the original metal tenors (e.g., Konnunaho et al., 2013).

## 3 THE Re-Os ISOTOPIC SYSTEM AND ITS USE IN STUDIES OF MAGMATIC Ni-Cu-PGE SULPHIDE DEPOSITS

#### **3.1 General principles**

Rhenium (Re) is a chemical element with an atomic number of 75, standard atomic weight of 186.207, density of 21.02 g/cm<sup>3</sup> and a hexagonal closed-packed crystal structure. It belongs to transition metal group number 7 of the periodic table. Rhenium has oxidation states from -1 to +7, with +4 and +7 dominating in nature. It is one of the rarest elements (< 1 ppb) in the Earth's crust (Shirey and Walker, 1998; Rumble, 2022)

Osmium (Os) belongs to platinum group elements (PGE). Its atomic number is Os is 76, standard atomic weight 190.23, density 22.59 g/cm<sup>3</sup> and crystal structure hexagonal closed-packed. Osmium shows oxidation states from -4 to +8 and in nature, 0, +3 and +4 states are prevalent. Like rhenium, osmium is among the rarest elements (<0.05 ppb) in the Earth's crust (Shirey and Walker, 1998; Rumble, 2022).

Both Os and Re are siderophile and chalcophile elements and are strongly partitioned into sulphides and metals rather than silicates. They were concentrated in the Earth's core and mantle during planetary formation (Shirey and Walker, 1998). Table 1 shows typical Re and Os concentrations and <sup>187</sup>Re/<sup>188</sup>Os ratios in different rock types and minerals.

In minerals, the following Re and Os partitioning behaviour is observed. Rhenium is incompatible into silicate and oxide minerals but strongly partitions into sulphides (e.g., Mallmann and O'Neill, 2007; Brenan et al., 2003; Righter and Hauri, 1998). According to Brenan (2008) and Fonseca et al. (2011), the sulphide melt-silicate melt partition coefficient of Os,  $D^{Os}$ , is of the order of  $10^4$ – $10^5$  for magmatic basaltic systems, and  $D^{Re}$  is about 400–800. Osmium is compatible into chromite as shown by Os concentrations varying from tens to more than 100 ppb (Table 1). Rhenium and Os show relatively high concentrations in organic-rich sediments (like black shales/schists), in which Re is strongly enriched over Os (see Table 1).

**Table 1.** Typical Re and Os concentrations and <sup>187</sup>Re/<sup>188</sup>Os ratios in terrestrial and extraterrestrial materials and minerals. Modified from Reiners et al. (2018), Carlson (2005), Mikulski and Stein (2007), Puchtel et al. (2020) Shirey and Walker (1998) and Stein et al. (1998).

Rocks	Re (ppb)	Os (ppb)	<sup>187</sup> Re/ <sup>188</sup> Os
C-chondrites	35–71	429–886	0.31–0.43
O-chondrites	26–89	289–1072	0.36–0.47
E-chondrites	24–76	277–861	0.41–0.44
Iron meteorites	35–4840	244-102000	0.32–0.99
Peridotite	0.009–1.77	0.003–9.2	0.03–27
Komatiite	0.37–3.65	0.75–2.47	0.9–14
Mid-ocean ridge basalt	0.16–1.2	<0.001-0.35	7–235
Ocean island basalt	0.02–1.6	<0.001-1.2	0.6–3000
Continental basalt	0.05–3.6	0.003–2.1	0.26–3150
Metalliferous sediment	0.04–11	0.002–1.5	1.2–112
Black shale	15–517	0.095–3.69	292–18780
Minerals			
Chromite	0.22–0.64	13–160	0.02–0.2
Molybdenite	700–160000	1.7-3536 (radiogenic)	Very high
Sulphides	52–2550	4.7–10000	0.24–104

During partial melting of mantle, Re is moderately incompatible and Os is highly compatible, leaving a mantle residue which is depleted in Re relative to Os (e.g., Morgan et al., 1981; Hauri, 2002; Walker et al., 1989). Consequently, mantle melts acquire high Re/Os ratios, which eventually leads to extreme fractionation in Re/Os between the mantle and crust.

Rhenium (Re) has two naturally occurring isotopes, of which <sup>185</sup>Re is stable and <sup>187</sup>Re radioactive. Osmium has seven naturally occurring isotopes, <sup>184</sup>Os, <sup>186</sup>Os, <sup>187</sup>Os, <sup>188</sup>Os, <sup>189</sup>Os, <sup>190</sup>Os, and <sup>192</sup>Os, of which <sup>184</sup>Os and <sup>186</sup>Os are radiogenic with extremely long half-lives and the rest are stable. <sup>187</sup>Os is the product of beta decay of <sup>187</sup>Re, with a decay constant of 1.666\*10<sup>-11</sup> a<sup>-1</sup> (Smoliar et al., 1996) and half-life of 4.16 \* 10<sup>10</sup> years. <sup>186</sup>Os is the decay product of long-lived radioactive isotope <sup>190</sup>Pt with a half-life of 4.69 \* 10<sup>11</sup> years. The Re-Os dating is based on the isochron method (Fig. 1).



Fig. 1. Graphical presentation of Re-Os isotopic fractionation and formation of an isochron.

By analysing multiple samples (for example, whole-rock samples and mineral separates) with variable Re/Os ratios, which are thought to have formed at same time and from the same parental magma, a Re-Os isochron can potentially be constructed. The Re-Os isochron equation is:

$$(187_{OS}/188_{OS_{sample present}}) = (187_{OS}/188_{OS_{initial}}) + (187_{Re}/188_{OS}) * (e^{\lambda t} - 1)$$
(1)

where t = the age of the sample,  $\lambda$  = the decay constant,  $(e^{\lambda t} - 1)$  = the slope of the Re-Os isochron. By resolving t, with regression slope calculation, the Re-Os isochron age for samples can be solved,  $t = \ln (a + 1)/\lambda$ , where a = the slope of the Re-Os isochron.

The initial Os isotopic composition can be presented by a gamma value,  $\gamma$ Os, which is the difference in percentage between the <sup>187</sup>Os/<sup>188</sup>Os ratio of the sample and that of chondritic meteorites at the time of formation of the sample. If a sample has positive  $\gamma$ Os, it implies that its Os came from a source with a long-term elevated <sup>187</sup>Re/<sup>188</sup>Os ratio and/or part of its Os was derived via contamination from crustal material with radiogenic Os. If a sample has a negative  $\gamma$ Os value, it implies that it came from a source with long-term low <sup>187</sup>Re/<sup>188</sup>Os, such as the subcontinental lithospheric mantle (Shirey and Walker, 1998). The following equation (Shirey and Walker, 1998) is used to calculate  $\gamma$ Os for samples:

$$\gamma Os_{(t)} = \left[ \left\{ \left( 187_{os} / 188_{os_{sample}(t)} \right) / \left( 187_{os} / 188_{os_{chon}(t)} \right) \right\} - 1 \right] * 100$$
(2)

Chondritic evolution is calculated from the most primitive initial Os compositions of the solar system (see above, average chondritic composition) with the following equation (Shirey and Walker, 1998):

$$(187_{OS}/188_{OS_{(t)}}) = (187_{OS}/188_{OS_{(initial)}}) + (187_{Re}/188_{OS_{(chon)}})(e^{\lambda(4.558*10^9)} - e^{\lambda t})$$
(3)

The  ${}^{187}$ Re/ ${}^{188}$ Os and  ${}^{187}$ Os/ ${}^{188}$ Os(i) ratios for chondrites are 0.40186 and 0.09517, respectively, (Shirey and Walker, 1998; Archer et al., 2014).

Two calculated model ages are used for the Re-Os isotope system.  $T_{MA}$  model age ( $T_{MA}$ ) is defined as the time of sample separation from mantle, and it is determined from the intersection of the evolution of the sample and that of chondritic mantle (Shirey and Walker, 1998). The following equation (4) defines how it is calculated (Shirey and Walker, 1998).

$$T_{MA} = 1/\lambda * ln \left\{ \left[ \left( (187_{OS}/188_{OS_{chon}}) - (187_{OS}/188_{OS_{sample}}) \right) \right. (4) \\ \left. \left. \left( (187_{Re}/188_{OS_{chon}}) - (187_{Re}/188_{OS_{sample}}) \right) \right] + 1 \right\}$$

 $T_{RD}$  model age ( $T_{RD}$ ) is defined as the time of Re depletion of a sample and it is determined from the intersection of the evolution of the sample, assuming its Re/Os ratio to be 0, and the chondritic mantle evolution. This model age represents a minimum age of Re depletion (Shirey and Walker, 1998).  $T_{RD}$  model age is calculated in two parts. First the Os isotopic composition is calculated at the eruption age (EA) (equation 5). Then the intersection time with chondritic mantle growth is calculated with assumption that previous melt-depletion event removed all the Re from the sample (Shirey and Walker, 1998) (equation 6).

$$(187_{OS}/188_{OS_{sample}(EA)}) = (187_{OS}/188_{OS_{sample}}) - (187_{Re}/188_{OS_{sample}})(e^{\lambda t} - 1)$$
(5)

$$T_{RD} = 1/\lambda * ln \left\{ \left[ \left( (187_{OS}/188_{OS_{chon}}) - (187_{OS}/188_{OS_{sample}(EA)}) \right) \right. (6) \\ \left. / (187_{Re}/188_{OS_{chon}}) \right] + 1 \right\}$$

In terms of geochemical behaviour, the Re-Os isotopic system is clearly different from the Sm-Nd, Rb-Sr, U-Pb and Lu-Hf isotopic systems because Os is compatible during mantle melting and has a high affinity to sulphide and metal phases, whereas the lithophile elements of the other isotope systems are incompatible during mantle melting and do not favour sulphides (with the exception of Pb) or metal phases. Both Re and Os prefer magmatic sulphide liquids, sulphide minerals, and chromite, and therefore the Re-Os system provides a good isotopic tool for dating

magmatic Ni-Cu-PGE deposits and obtaining genetic information on ore-forming processes, including the source of Os and, by inference, other highly chalcophile elements (e.g., Barnes and Ripley, 2016; Lambert et al., 1998, 1999a, 2000; Shirey and Walker, 1998; Walker et al., 1994, 1997).

Due to the high Re/Os ratios, crustal rocks develop radiogenetic Os isotopic composition (positive  $\gamma$ Os) over time. If mantle-derived magmas interact with crust, and in especially with Re and Os rich sediments during or after their emplacement, their <sup>187</sup>Os/<sup>188</sup>Os ratios may increase significantly. Therefore, the Os isotope compositions are sensitive indicators of crustal contamination during the formation of magmatic Ni-Cu-PGE sulphide deposits. For determining the initial Os composition of ultramafic rocks, primitive magmatic minerals, such as chromite and/or olivine have been used, because these minerals contain little Re and thus have a low <sup>187</sup>Re/<sup>188</sup>Os ratio (e.g., Gangopadhyay and Walker, 2003; Puchtel et al., 2020). When using the Re-Os isotopic system for dating, these minerals need to be coupled with other minerals or whole-rock samples with higher Re/Os ratios.

#### 3.2 R factor

The R factor, which was originally defined by Campbell and Naldrett (1979), is the ratio between the mass of silicate liquid to the mass of sulphide liquid. It can be used to model the composition of a sulphide liquid which segregates from a silicate liquid. High R factor values mean that a large amount of silicate liquid has equilibrated with a small amount of sulphide liquid. In contrast, low R factor values indicate that a relatively large amount of sulphide liquid has equilibrated with a relatively small amount of silicate liquid (e.g., Campbell and Naldrett, 1979; Naldrett, 2004). Below is an equation (Campbell and Naldrett, 1979), which shows how the chalcophile element concentration of sulphide liquid depends on the R factor and the silicate melt composition.

$$C_{S} = \frac{[C_{L} * D * (R+1)]}{(R+D)}$$
(7)

where  $C_S$  = the concentration of metal in the sulphide liquid,  $C_L$  = concentration of metal in silicate liquid, D = partition coefficient of metal between the sulphide and silicate liquids, R = the mass of silicate magma from which the sulphide collects the metal (the mass ratio of silicate to sulphide liquid). The calculated R factor values are usually high, well above 1000, in large PGE-enriched magmatic systems, such as ores related to flood basalts and layered intrusions. For example, in the Siberian flood basalt province, the estimated R factors range from 1000 to 5000 for Talnakh ores and exceed 10 000 for Noril'sk ores (Duran et al., 2017; Lambert et al., 1999b; Naldrett, 2004; Naldrett et al., 1999). In large layered intrusions, the estimated R factor values fall generally in the range of 10 000–100 000, being, for example, around 10 000 and 100 000 for the Merensky PGE Reef and the UG-2 PGE reef of the Bushveld Complex, respectively (Barnes and Maier, 1999; Naldrett, 2004). Deposits generated in less voluminous magmatic systems, such as komatilitic deposits and base metal-dominated sulphide deposits, show generally lower R factor values, usually approximately 100–1000. For example, komatilitic massive sulphide ores at Kambalda have estimated R factors in the range of 100–500 (Lesher and Barnes, 2008 and references therein; Lesher and Campbell, 1993) and komatilitic basalt-hosted Raglan sulphide ores values between 300 and 1100 (Lesher and Barnes, 2008 and references therein; Barnes and Picard, 1993). In the Sudbury ores, the R factor values are between 140 and 1200. Törmänen et al (2016) assessed that in the Lomalampi komatilite-hosted PGE-(Ni-Cu) deposit, the R factor was between 500 and 1000.

Lambert et al. (1998) evaluated the effects of the R factor and crustal contamination on the Kambalda sulphide deposit by using the isotope data from Foster et al. (1996). They concluded that the ores were not formed by extensive assimilation of sedimentary country rocks, though crustal contamination of komatilitic lava flows cannot be fully rejected, if the contaminant has a non-radiogenic Os isotopic composition and low Re and Os concentrations, and the R factor was high enough (above 2000). In contrast, Lesher and Burnham (2001) used a multicomponent elemental and isotopic mass balance equation to model batch equilibrium in magmatic Ni-Cu-PGE systems and concluded that sediment melting and assimilation by a komatiitic magma in the Kambalda area was an important factor in the generation of the sulphide deposits, and the sulphur isotope composition of Kambalda sulphides is a more sensitive indicator of contamination than the Re-Os isotopes. One possible reason for this is that Os and S occur in different abundances in sulphide and silicate melts. Osmium is a trace component in sulphide melt and an ultra-trace component in the silicate melt and therefore will be less sensitive to crustal contamination than S, which is a major element in sulphide melt and trace element in silicate melt (Lesher and Burnham, 2001). More recently, Staude et al. (2016, 2017) produced textural evidence that the Kambalda sulphide ores were formed by thermomechanical erosion and assimilation of sulphide-bearing footwall sedimentary rocks, and this is their favoured genetic model for the Kambalda sulphide ores.

Magmatic ore-forming systems can be highly dynamic and R factor with other parameters vary and affect the Os isotopic composition of sulphides. Lesher and Burnham (2001) modelled R' factor (which is analogous to R factor, but has more variables) under closed-system conditions using Kambalda komatiites as an example (Fig. 2.). They considered the following four models: 1) In systems without an external S-bearing contaminant,  $\gamma Os$ ,  $\delta^{34}S$  and S/Se do not vary with R' factor and the system will preserve its original Os isotope composition. 2) In systems with addition of external sulphur,  $\gamma Os$ ,  $\delta^{34}S$  and S/Se increase with decreasing R' factor, reflecting the increasing relative contribution from the crustal component. 3) Osmium and sulphur are present in different amounts in magmatic systems, and therefore the behaviour of yOs is different compared to that of  $\delta^{34}$ S and S/Se. If everything else is equal in the system, Os (which is trace element in sulphide melt and ultra-trace element in silicate melt) is a less sensitive indicator of crustal contamination than S, which is a major element in sulphide melt and trace element in silicate melt, but if the contaminant has a high Os concentration, the Os isotope composition could be a more sensitive indicator of crustal contamination than the S isotope composition. 4) Adding phases to the system changes the mass balance and therefore in most cases dilutes the contaminant and isotopic signal of contamination. In summary, if everything else is equal, the system is closed and has no contamination, no isotopic fractionation accompanies the process and yOs stays constant with varying R' factor (Fig. 2) (Barnes and Ripley, 2016). On the other hand, the effects of contamination on yOs decreases with increasing R'. Because natural systems are rarely in perfect equilibrium and are highly dynamic with varying R factor and other parameters, it is also important to use other isotopes, such as those of S, Sr, Nd, to assess the degree of contamination in magmatic Ni-Cu-PGE deposits.



Fig. 2. Modelled  $\gamma$ Os as a function of R' factor compared with measured  $\gamma$ Os in Kambalda sulphide ores (modified from Lesher and Burnham, 2001). The curves represent models with different relative mass-proportions of sulphide : sulphide xenomelt (sulphide xenomelt is formed from S-bearing contaminant melting) : restite/residue : olivine. Models with no change in  $\gamma$ Os value are 1:0:0:0 and 1:0:0:60, which represents fractional crystallisation of sulphide and sulphide + olivine, respectively, without any external S-bearing contamination. The other models represent contamination with metal- and S-bearing sediments (with  $\gamma$ Os +900) with variable amounts of crystallisation of olivine.

#### 3.3 Applications to Ni-Cu-PGE sulphide deposits

Sulphur isotopes can give information on magmatic ore-forming processes, especially the source of sulphur, which is one of the key factors in the formation of magmatic sulphide deposits. Sulphur isotopes are usually studied together with Os isotopes and combining information from both isotope systems helps to understand magmatic processes, especially contamination of magmas. Seat et al. (2009) have concluded that based on sulphur isotope data from the Nebo-Babel deposit, mantle-derived sulphur alone may be sufficient for the formation of a Ni-Cu sulphide ore deposit in some cases. The study by Ripley and Li (2013) demonstrated that sulphide saturation in maficultramafic magmas and formation of a Ni-Cu-PGE ore deposit can occur in large-volume, highly dynamic open systems (e.g., magmatic feeder conduit systems or large-volume flood basalts), where the sulphide collection process is highly effective. Recent studies of multiple sulphur isotopes of komatiite-hosted Ni-Cu-PGE sulphide deposits have shown that contamination with sulphur-bearing country rock (for example, black schist, VMS) played an important role in the origin of these deposits (Bekker et al., 2009; Fiorentini et al., 2012; Konnunaho et al., 2013).

Many world-class magmatic ore deposits and their host intrusions or lava flows have been studied using the Re-Os isotope system, including the Sudbury Igneous Complex Canada, Voisey's Bay (Canada), Eagle Ni-Cu deposit (Canada), Alexo, Texmont and Hart deposits (Canada), Pechenga and Noril'sk-Talnakh Ni-Cu-PGE deposits (Russia), Stillwater Complex (United States), Great Dyke (Zimbabwe), Bushveld Complex (South Africa), Kambalda deposit (Australia) and many Chinese deposits. Reviews of these studies can be found in Barnes and Ripley (2016) and Lu et al. (2019). Below is presented a selection of studies in which the Re-Os system has been applied to magmatic Ni-Cu-PGE deposits.

One of the first applications of the Re-Os isotopic system to magmatic ore deposits was the study of Sudbury Ni-Cu ores by Walker et al. (1991). They concluded that these ores include a substantial proportion of Os from crustal rocks. Subsequently, Dickin et al. (1992) and Morgan et al. (2002) confirmed the presence of highly radiogenic Os (positive  $\gamma$ Os varying from +346 ± 10 to 375 ± 12) in Sudbury, and Morgan et al. (2002) obtained a Re-Os isochron age of 1835 ± 70 Ma for Sudbury ores, which is in agreement with the U-Pb age of 1850 ± 1 Ma (Krogh et al., 1984). An important conclusion from all these studied is that a significant part of the Os in the Sudbury ores is derived from crustal rocks, which is compatible with the general concept that the Sudbury intrusion represents an impact melt sheet (Barnes and Ripley, 2016).

The Norilsk-Talnakh ore deposits were studied by Walker et al. (1994) and Malitch and Latypov (2011), with both works presenting Re-Os isochron ages for deposits, which agree with the U-Pb zircon ages of ~247 Ma. Initial  $\gamma$ Os compositions show some variation from +0.4 to +12.9, which was explained by the deep mantle source of magmas having incorporated ancient Re-enriched crustal material or by a very low amount of crustal contamination, or contamination with anhydrite, which have low Re and Os concentrations. In their study of komatiites from Kambalda, Lesher and Burnham (2001) concluded that due to mass balance constraints, Os isotope compositions of magma may be reset to near-chondritic values and S isotopes are little affected if replenishment of new uncontaminated mantle-derived magma remove early-formed sulphides upstream, which reequilibrate with replenished magma in a highly dynamic open system conduit-type magmatic environment. This process could influence isotopic values more significantly for a trace component, such as Os, than for a major element, such as S, masking the effects of the earlier high degrees of contamination (Lesher and Burnham, 2001). This masking effect could also explain the near-chondritic Re-Os isotopic compositions of the Noril'sk-Talnakh deposits.

Based on the Re-Os isotope data from the Pechenga Ni-Cu ore deposits, Walker et al. (1997) concluded that all mineralised intrusions show evidence for crustal contamination. For example, the initial  $\gamma$ Os values for primary magmatic sulphides in the Pilgujärvi intrusion have an average  $\gamma$ Os value of +46 and other ore-bearing intrusions, such the Kammikivi sill, show  $\gamma$ Os values as high as +251. They also observed that some of the whole-rock samples of both mineralised and

sulphide-poor intrusions were affected by post-magmatic metamorphic alteration events at about 1.7–1.8 Ga. Because of this open-system behaviour in many whole-rock samples, they proposed that primary igneous minerals, such as chromite, olivine, clinopyroxene, and primary sulphides, should be used for analysis of Re-Os isotopes for these rocks. Hanski et al. (2011) studied the Pahtajärvi ultramafic dyke which occurs in the underlying volcanic formation and acted as a feeder conduit to ore-bearing intrusions. The obtained Os isotope data from sulphide separates ( $\gamma$ Os in the range of +52 to +69) demonstrate that a significant component of radiogenic Os was present in the magma.

The Voisey's Bay ore deposit was studied by Lambert et al. (1999a, 2000) and their conclusion was that there were multi-stage processes of mineralisation. The Re-Os isochron age of  $1323 \pm 135$  Ma obtained for massive and disseminated sulphide samples is the same, within error, as the U-Pb zircon age of  $1332.7 \pm 1$  Ma (Amelin et al., 1999). An interesting finding is the highly radiogenic initial Os isotope composition ( $\gamma$ Os +1040  $\pm$  200), which indicates extensive contamination with old crustal material. Lambert et al. (2000) suggested two staging areas within the crust, where contamination of primitive magmas occurred before entering the upper Voisey's Bay chamber. First a high-Mg basaltic magma was contaminated with lower-middle crust mafic orthogneisses, which was followed by more extensive contamination in the upper crust with sulphidic-graphitic gneiss in magma conduits and/or in the Reid Brook subchamber. Compositions of disseminated sulphide-bearing intrusive rocks produced a scattered pattern in the Re-Os isochron plot, which Lambert et al. (2000) interpreted as a result of variable degrees of mixing with country rocks. Sulphide mineral separates from massive sulphide samples defined a Re-Os isochron with an age of 1004  $\pm$  20 Ma, which corresponds to the timing of the Grenville orogeny, indicating resetting of the sulphide system in orogenic hydrothermal alteration processes.

Lahaye et al. (2001) studied the effects of metamorphism and R factor on the Re-Os isotope compositions of 2.7 Ga komatiitic lava flows (Alexo, Texmont and Hart) and related Ni-Cu sulphide deposits in the Abitibi greenstone belt, Canada. Their data suggest that the Alexo lava flow was contaminated with crustal material, and both in the Alexo and Hart lava flows, remobilisation of Re and Os in sulphides by hydrothermal fluids occurred during the Grenville orogeny at ca. 1.2 Ga. In contrast, the Texmont lava flow was not affected by this kind of localised hydrothermal alteration. They also concluded that sulphide saturation was caused by assimilation of sulphide-bearing sedimentary rocks, and that the Re-Os isotopic heterogeneity of the Abitibi sulphides is best explained by variable R factors. Later, Gangopadhyay and Walker (2003) studied the Alexo lava flow and concluded that magmatic behaviour of Re and Os is preserved in non-mineralised whole-rock samples. This all indicate that Re-Os isotope results from magmatic

sulphide-bearing systems must be interpreted with careful consideration of different magmatic and post-magmatic processes.

Using disseminated, semi-massive, massive and whole-rock samples, Ding et al. (2012) obtained a Re-Os isochron age of  $1106 \pm 34$  Ma for the Eagle intrusion-hosted Ni-Cu-PGE deposit. This Re-Os age is in good agreement with the U-Pb age of  $1107 \pm 2$  Ma (Ding et al., 2010). They also calculated an initial  $\gamma$ Os value of +34, which is explained by a low degree of contamination (~3% contamination of picritic magma with country rocks). This low amount of crustal contamination could also be explained by exchange reactions in a magma conduit, where early-formed sulphides and non-contaminated magma could mask evidence for an earlier higher degree of crustal contamination (Ding et al., 2012).

Several studies have been conducted on the Stillwater Complex and related PGE reefs using the Re-Os isotope method (e.g., Lambert et al., 1989, 1994; Martin, 1989; Marcantonio et al., 1993; Horan et al., 2001). The following conclusions have been made. The Re-Os age of 2740 Ma obtained for molybdenite (Marcantonio et al., 1993) is in agreement with the accepted age of the intrusion. Two sources of Os can be recognised, which is consistent with other petrogenetic research that indicate that two magmas were involved in the formation of the Stillwater Complex: an ultramafic magma, which shows weak signatures of crustal contamination, and maficanorthositic magma, which records signs of contamination with Archaean crust. Lambert et al. (1994) reported radiogenic  $\gamma$ Os values of +12 to +34 for PGE-enriched units (B chromitite seam and J-M Reef) and near-chondritic  $\gamma$ Os values of -2 to +4 for PGE-poor chromitites. Mixing of an ultramafic magma with a mafic magma is proposed to be the cause for positive radiogenic  $\gamma$ Os values and the formation of the PGE-enriched J-M Reef. Chromite separates from chromitite seams and ultramafic series were analysed by Horan et al. (2001). They obtained initial  $\gamma$ Os values ranging from +2 to +16.4, also suggesting the presence of two magmas, one with a near-chondritic Os isotopic composition and the other with a radiogenic Os composition indicative of contamination with sedimentary rocks below the Stillwater Complex. Martin (1989) also concluded that contamination of a chondritic mantle-derived melt with mafic-intermediate crustal material has occurred at Stillwater. Marcantonio et al. (1993) also investigated chromites and came to the conclusion that chromites from the ultramafic series had crystallised from a mantle-derived magma that had not been contaminated much with continental crust and the slight scattering in the Os isotopic data was a result of hydrothermal alteration processes.

Employing chromite separates, Schoenberg et al. (2003) obtained an imprecise Re-Os isochron age of  $2580 \pm 500$  Ma for the Great Dyke, which agrees with the previous U-Pb zircon age of  $2574 \pm 2$  Ma (Wingate, 2000). They concluded from mixing calculations that 0–33% of Os in chromites

is crustal in origin. Osmium isotope data combined with other isotopic systems could be used to suggest that the source magmas underwent no interaction with subcontinental lithospheric mantle and parental magmas were plume-derived with a heterogenous Os isotopic composition.

Many Re-Os isotope studies have been made from the Bushveld Complex, using chromite, sulphides, pyroxenes and different alloys to unravel the genesis of the PGE enrichment in the UG2 chromitite, Merensky Reef and Platreef (McCandless and Ruiz, 1991; Schoenberg et al., 1999; Hart and Kinloch, 1989; Reisberg et al., 2011). All these investigations indicate that the parental magma of the complex was contaminated by variable degrees with crustal material, consistent with other isotopic systems. The produced Re-Os isochron ages for pyroxenite samples are  $2011 \pm 51$  Ma (Reisberg et al., 2011) and  $2043 \pm 11$  Ma (Schoenberg et al., 1999), which fit within uncertainty with the approved Bushveld Complex age, as based on the very precise U-Pb zircon and baddeleyite ages of  $2055.54 \pm 0.27$  Ma (Merensky Reef) and  $2056.28 \pm 0.15$  Ma (UG1) (Mungall et al., 2016).

Recently, many Chinese Ni-Cu-PGE deposits have been studied using Re-Os isotopes, with a summary of these investigations being presented by Lu et al. (2019). For example, Han et al. (2007) determined a Re-Os isochron age  $305 \pm 15$  Ma for the Kalatongke Cu-Ni deposit by using massive and densely disseminated ore samples, which is consistent with the U-Pb zircon age of  $287 \pm 5$  Ma of the deposit (Han et al., 2004). In contrast, Qu et al. (2013) obtained a clearly older Re-Os pseudo-isochron age of  $433 \pm 31$  Ma for disseminated sulphide ore samples. According to them, silicate minerals in disseminated sulphide samples prohibit the diffusion of Os between the sulphide minerals. Thus, equilibration of the Os isotopic compositions among the sulphide minerals could not be achieved and consequently they preserved the heterogeneities in their compositions that were caused by crustal contamination. Because of this, the disseminated sulphide samples yielded a pseudo-isochron whereas the massive sulphide samples gave a geologically meaningful isochron age. Yang et al. (2008) came to a similar conclusion from their studies of the Jinchuan deposit. Yang et al. (2014) obtained a Re-Os isochron age of  $431 \pm 19$  Ma for sulphide-bearing samples from the Poyi and Poshi intrusions, which occur in the same Northern Xinjiang area as the Kalatongke intrusion.

Lu et al. (2019) published a review paper on geochemistry and genesis of magmatic Ni-Cu-PGE deposits in China. Most of the samples from the Chinese deposits are high in  $\gamma$ Os (>+20) and  $\epsilon$ Nd varies between between -3 and +8 (Fig. 3), except for the Jinchuan deposit. According to Lu et al. (2019),  $\gamma$ Os and  $\epsilon$ Nd values of most of these deposits plot on a mixing trend between magma compositions derived from a pyroxenitic mantle source and continental crust, and similar compositions are observed samples for the Voisey's Bay and Eagle deposits (Fig. 3). Compositions

of komatiite-related deposits plot in a low- $\gamma$ Os (<10) and intermediate- $\epsilon$ Nd area, which is on a mixing trend between peridotitic mantle-derived magmas and continental crust (Lu et al., 2019). Considering other Chinese deposits, the Jinchuan samples show lower  $\epsilon$ Nd and equally high  $\gamma$ Os, indicating that magmas have isotopic compositions on a mixing trend between a peridotitic-pyroxenitic mantle magma and continental crust. Lu et al. (2019) came to the conclusion that all Chinese Ni-Cu-PGE deposits have higher  $\gamma$ Os than deposits with parental magmas from a peridotitic mantle source (e.g., Raglan, Alexo, Kambalda, Thompson). In contrast, the magmas representing isotopic mixtures of pyroxenitic mantle and continental crust, suggests a pyroxenitic magma source for Os in the Chinese deposits.



**Fig. 3.**  $\epsilon$ Nd vs.  $\gamma$ Os diagram for Ni-Cu-PGE deposits, including data for the Kevitsa (Ni-PGE and Normal Ore, from Hanski et al., 1997) and Sakatti deposits from this study and Brownscombe (2016). Modified and references for data sources from Lu et al. (2019). Abbreviations: BMZ = Baimazhai; EMI and EMII = enriched mantle I and II, which are ocean island basalt end-members; HSN = Heishan; HSD = Huangshandong; HQL = Hongqiling; JBS = Jinbaoshan; JC = Jinchuan; JBLK = Jingbulake; KLTK = Kalatongke; LMH = Limahe; PHC = Piaohechuan; PB = Pobei; SCLM = subcontinental litospheric mantle; TY = Tianyu; VB = Voiseys Bay; XRHM = Xiarihamu; ZA = Zhouan.

The layered intrusions and associated magmatic ore deposits that were studied in northern Finland using Re-Os isotopes include the Kevitsa intrusion (Hanski et al., 1997), the Koitelainen and Akanvaara intrusions (Hanski et al., 2001a), and the Kemi intrusion (Yang et al., 2016). Based on Nd and Os isotopes, Hanski et al. (1997) concluded that varying contribution of these elements from crustal sources (sulphur- and carbon-bearing pelitic sediments), together with varying silicate liquid/sulphide liquid ratio partly explains the large chalcophile element fractionation in the Kevitsa Ni-Cu-PGE ores. Yang et al. (2016) found that chromite separates from the Monchepluton and Kemi intrusions have nearly chondritic  $\gamma$ Os compositions, similarly to the coeval Vetreny belt komatiites, and concluded that due to the Os-rich nature of the parental magmas, the Os isotope compositions of the magmas were not significantly changed by crustal contamination. Gangopadhyay et al. (2006) and more recently Puchtel et al. (2020) published Re-Os isotope data for 2.06 Ga komatiites from the Central Lapland greenstone belt. Utilizing chromite separates, they were able to define precisely the initial Os isotope composition of this magmatism, which turned out to be very close to chondritic, providing important background information for studies of komatiite-related sulphide mineralisation in Lapland, including the Lomalampi deposit.

#### 3.4 Limitations of the Re-Os isotopic system

The Re-Os isotope system as a geochronological tool has its limitations. Mobilisation of Re during post-magmatic alteration processes can lead to its loss or gain, which is manifested by a considerable scatter in <sup>187</sup>Re/<sup>188</sup>Os vs. <sup>187</sup>Os/<sup>188</sup>Os isochron plots (e.g., Gangopadhyay et al., 2005; Moilanen et al., 2019; Arndt et al., 2008). Typically, Re-Os ages need to be confirmed with other age determination methods (e.g., U-Pb, Sm-Nd). One problem with the application of the U-Pb zircon method to ultramafic rocks is that zircon is not a common mineral in these rocks, which have crystallised from primitive magmas (e.g., komatiites), and usually indirect U-Pb zircon age determinations, for example, from gabbroic dykes crosscutting ultramafic rocks are used.

To avoid complications due to open-system behaviour of whole-rock samples, separates of primary magmatic minerals can be used, but it is not always easy to extract pure minerals; for example, sulphide inclusions in silicate or oxide separates (e.g., chromite, olivine) or metamorphically altered chromite with secondary magnetite rims may cause complications in the Re-Os results. One possibility is to use a micro-drilling technique, laser, or focused ion beam (e.g., Keir-Sage et al., 2021; Wirth, 2009) to cut, for example, a pure fresh chromite core from a thick section (~100  $\mu$ m) sample to get a possibly pristine initial Re-Os isotopic composition. This method would be time consuming, and the grain size needs to be large enough. Another method

could be to apply acid leaching to chromite-magnetite grains to dissolve some of the secondary magnetite rim around chromite grains. To improve the potential to obtain proper isochron ages, chromite separates could be coupled with some other mineral grains and/or whole-rock samples with variable and high Re/Os from the ultramafic olivine-chromite cumulate rocks and also sulphides from mineralised parts of an intrusion. Later, when better reference materials for different minerals with low Re and Os concentrations and corrections methods for the overlap of <sup>187</sup>Re on <sup>187</sup>Os are available, in-situ LA-ICP-MS or some other method (such as laser ablation-tandem ICP-MS or atom probe tomography) could also be one possibility to analyse chromite and sulphide grains (e.g., Selby and Creaser, 2004; Bragagni et al., 2018; Hogmalm et al., 2019). However, some caution should be exercised when interpreting Re-Os geochronological results, especially if there is no information on the age of the deposit from other age dating methods.

#### **4 TRACE ELEMENT COMPOSITION OF IRON OXIDES**

#### 4.1 Oxide minerals in magmatic Ni-Cu-PGE sulphide systems

The main sulphide minerals in magmatic Ni-Cu-PGE deposits typically consist of pyrrhotite, pentlandite, chalcopyrite, and occasionally minor pyrite (Naldrett, 2004). They are commonly associated with some amount of iron oxides due of the capability of sulphide liquid to dissolve oxygen. Magnetite or Cr-magnetite can crystallise together with early-forming Fe-rich monosulphide solid solution (MSS), and after MSS crystallisation, at lower temperatures, with Cu-rich intermediate solid solution (ISS) (e.g., Naldrett, 2004; Dare et al., 2012). How much oxygen is dissolved in a sulphide liquid is dependent on the conditions and the metal content of the sulphide liquid: the solubility increases with increasing oxygen fugacity (fO<sub>2</sub>) and iron content and decreases with increasing nickel (Ni) and copper (Cu) contents, with the role of Ni being more important than that of Cu in decreasing the oxygen solubility in the system (e.g., Lee, 1999; Fonseca et al., 2008).

Chrome spinel (see Fig. 4) is the first liquidus phase in mafic-ultramafic magmas with the exception of high-Mg komatiites, in which olivine precedes spinel (Barnes and Roeder, 2001). Ewers et al. (1976) proposed that Cr-bearing spinels crystallise directly from a sulphide liquid, but later Fonseca et al. (2008) re-evaluated this view. They concluded that direct crystallisation of chromite from a sulphide liquid is inconsistent with the fact that Cr-bearing spinels in the Kambalda ore deposits are not found in sulphide ore, which would be the case if they crystallised directly from sulphide liquid, but they are concentrated near the sulphide-silicate liquid boundaries. Fonseca et al. (2008) proposed that the mechanism behind this phenomenon is the

interaction between silicate and sulphide liquids at the silicate-sulphide liquid boundary where diffusion of oxygen out of the sulphide liquid can lead to precipitation of magnetite and/or chromite/Cr-magnetite (e.g., Frost and Groves, 1989; Fonseca et al., 2008). Based on these observations, Cr-magnetite and magnetite can form as primary minerals from sulphide liquids in mafic-ultramafic systems.



**Fig. 4.** Back-scattered electron images of chromite grains from studied komatiite-hosted sulphide deposits. A) Subhedral chromite grains from the Lomalampi PGE-(Ni-Cu) deposit. Note the base metal sulphide inclusions. B) Anhedral, altered chromite grain from the Tulppio Ni-PGE mineralisation. C) Anhedral and subhedral chromite grains from the Ruossakero Ni-(Cu) deposit. D) Well-preserved euhedral chromite grain from the Vaara Ni-(Cu-PGE) deposit. E) Highly altered, subhedral chromite grain from the Tainiovaara Ni-(Cu-PGE) deposit. F) Highly altered, subhedral chromite grains in a non-mineralised komatiite lava flow from the Kovero area. Figure is taken from Moilanen et al. (2019).

Another option for the generation of oxides in sulphide systems is secondary oxide formation by post-magmatic hydrothermal oxidation of sulphides or other secondary processes. A good example is the Vaara deposit, where most of the oxides are formed after oxidation of sulphides to magnetite via post-magmatic hydrothermal processes (Konnunaho et al., 2013) (Fig. 5C). In the Jinchuan deposit, a major part of the oxides is also secondary (Yang et al., 2018). Figure 5 shows examples of images of magnetites from the studied Ni-Cu-PGE deposits.



**Fig. 5.** Photomicrographs (A–D) and back-scattered electron images (E and F) of magnetite grains from studied Ni-Cu-PGE deposits. A) Massive sulphide with euhedral magnetite grains from the Hietaharju deposit. B) Disseminated and sheared sulphides with magnetite and Cr-magnetite from the Hietaharju deposit. C) Sulphide globule partly replaced by magnetite from the Vaara deposit. D) Disseminated sulphides with Cr-magnetite and magnetite from the Tainiovaara. E) Disseminated and remobilised sulphides with zoned Cr-magnetite from the Ruossakero deposit. F) Disseminated sulphides with magnetite from the Lomalampi deposit. Abbreviations: CPY = chalcopyrite, Cr-MGT = Cr-magnetite, MGT = magnetite, MIL = millerite, PN = pentlandite, PO = pyrrhotite, PY = pyrite, VIOL = violarite. Figure taken from Moilanen et al. (2020).

#### 4.2 Oxide compositions

Compositions of spinels and particularly chromite in mafic-ultramafic rocks have been used as a petrogenetic indicator for a long time (e.g., Irvine, 1965; Barnes and Roeder, 2001), and they have also been tried to employ as an exploration tool (e.g., Groves et al., 1977; Locmelis et al., 2013; Locmelis et al., 2018). Groves et al. (1977) suggested that the zinc concentration of chromite could potentially be used as an exploration tool for Ni deposits, because a high Zn content could be an indication of contamination of komatiitic magma with sedimentary rocks. Zinc in chromite has also drawn attention by researchers studying Svecofennian Ni-Cu deposits in Finland (Peltonen and Lamberg, 1991; Peltonen, 1995). However, later studies have shown that applying the Zn content of chromite as an exploration tool for komatiitic Ni deposits has a low potential due to metamorphic equilibrium reactions of chromite, which changes the chromite composition (e.g., Barnes, 2000).

Iron oxides, such as magnetite, can incorporate a wide range of different cations replacing Fe<sup>2+</sup> and Fe<sup>3+</sup> in their lattice. Thus, the trace element characteristics of magnetite can provide an indication of the composition of the silicate or sulphide melt from which it has crystallised. Magnetite compositions of the Sudbury ore deposits have revealed that all lithophile elements (e.g., Cr, Ti, V, Al, Mn, Sc, Nb, Ga, Ge, Ta, Hf, W and Zr) are compatible into magnetite crystallised from sulphide liquid and the concentrations of these elements vary as a function of the degree of fractionation of the sulphide liquid (fractionation from MSS to ISS) (Dare et al., 2012). Different compositions of magnetite from different ore deposit types have also been observed. According to Dupuis and Beaudoin (2011), magnetite in Ni-Cu-PGE sulphide deposits is characterised by relatively high Ni and Cr contents when compared with magnetite compositions from hydrothermal and sedimentary ore deposits is a feature supporting their formation during sulphide crystallisation (Boutroy et al., 2014).

Recently, several discrimination diagrams have been proposed to determine the origin of magnetite based on its trace element composition. Dare et al. (2014) presented a Ni/Cr vs. Ti diagram, which discriminates between magmatic and hydrothermal magnetite, and Dupuis and Beaudoin (2011) introduced a Cr + Ni vs. Si + Mg diagram to distinguish magnetite from Ni-Cu-PGE ore deposits and other deposit types. Ward et al. (2018) used a Cr/V ratio vs. Ni diagram to differentiate magnetite from mineralised and barren mafic-ultramafic rocks. Liu et al. (2015) in turn presented a Ga+Co vs. Ge diagram to discriminate magnetite from Ni-Cu ore deposits, massif-type anorthosites and evolved parts of mafic layered intrusions.

As mentioned before, the composition of chromite/spinel can be useful in mineral exploration for magmatic sulphide deposits (Barnes and Roeder, 2001 and references therein). For example, the current study by Locmelis et al. (2018) shows that the Ru (or other PGE) concentration in chromite is indicative of the presence or absence of a sulphide liquid during the time of chromite crystallisation. They concluded that two groups of chromite can be distinguished based on their Ru contents, which correspond to the sulphide saturation state of the magma during chromite crystallisation. It was shown that chromite grains crystallised from sulphide-undersaturated magmas contain >150 ppb Ru, while chromite grains crystallised from sulphide-saturated magmas mostly have <150 ppb Ru.

#### **5 ANALYTICAL METHODS**

In this study, isotopic compositions of Re and Os for article II were measured at the Key Re-Os Laboratory of China, the Academy of Geological Sciences, Beijing, China, using negative thermal ionisation mass spectrometry (N-TIMS). The samples were first loaded into Carius tubes together with <sup>185</sup>Re and <sup>190</sup>Os spikes and digested by reverse aqua regia in the presence of a small amount of  $H_2O_2$  (Shirey and Walker, 1998). After this, the tubes were heated in an oven at 230 Celsius degrees for about 24 hours. Osmium was separated as  $OsO_4$  by distillation at 105-110 °C and trapping by Milli-Q water. During distillation, the reverse aqua regia acted as an oxidiser. Rhenium was extracted from the residue by acetone in a 5 M NaOH solution.

For article III, isotope analyses were conducted at the University of Maryland, USA, using N-TIMS for Os isotopes in the Isotope Geochemistry Laboratory and multi-collector inductivelycoupled plasma mass-spectrometry (MC-ICP-MS) for Re isotopes in the Plasma Laboratory. The sample preparation included digestion in Carius tubes and Re and Os separation from the obtained solution employing solvent extraction and ion exchange columns. Detailed descriptions of the Re-Os analytical methods can be found from articles II and III (Moilanen et al., 2019; 2021).

In-situ iron oxide compositions were determined with electron probe microanalyzer (EPMA) at the Centre of Material Analysis, University of Oulu, and laser ablation-single collector-inductively coupled plasma-mass spectrometry (LA-SC-ICP-MS) in the Finnish Geosciences Research Laboratory (SGL), which is a joint facility of the Geological Survey of Finland (GTK) and the geoscience departments of Finnish universities in GTK, Espoo. Trace element concentrations of oxide grains were measured from the same areas previously analysed by EPMA, and EPMA-derived Fe was used as an internal standard element.

#### **6 RESEARCH TARGETS**

In Finland, the past mining of Ni-Cu-(Co) sulphide ore deposits has mainly been focused on deposits related to the 1.88 Ga Svecofennian orogenic magmatism in the southern part of Finland (Haapala and Papunen, 2015). Only one Archaean komatiite-related sulphide deposit, Tainiovaara in eastern Finland, has been mined in a small-scale operation in the late 1980's (Konnunaho et al., 2015), though several small komatiite-hosted Ni-Cu-PGE sulphide deposits are known to occur in both Palaeoproterozoic and Archaean greenstone belts in the eastern and northern parts of the country (Konnunaho et al., 2015). In addition, in the Central Lapland greenstone belt, the disseminated Ni-Cu-PGE sulphide deposit hosted by the ~2.06 Ga Kevitsa mafic-ultramafic intrusion is presently mined (Boliden, 2021). Another significant, so-far unexploited deposit is the Sakatti Cu-Ni-PGE sulphide deposit (Ahvenjärvi, 2015; Barron, 2020; Brownscombe et al., 2015; Fröhlich et al., 2021; Silventoinen, 2020; Vuorisalo, 2021), which is located in Central Finnish Lapland, not far from the Kevitsa deposit.

Magmatic Ni-Cu-PGE deposits hosted by mafic-ultramafic rocks occur both in Archaean and Palaeoproterozoic greenstone belts in Finland (Fig. 6). In this study, we have applied the Re-Os isotope system and iron oxide trace element chemistry to the following Ni-Cu-PGE deposits in northern and eastern Finland. The Archaean deposits include the Ruossakero Ni-(Cu) deposit in the Enontekiö-Käsivarsi area in Finnish Lapland, the Vaara and Hietaharju Ni-(Cu-PGE) deposits in the Suomussalmi greenstone belt in eastern Finland, and the Tainiovaara Ni-(Cu-PGE) deposit occurring in a small greenstone belt relict in eastern Finland. Also, an Archaean dunite body and related low-grade Ni-(PGE) mineralisation at Tulppio in eastern Lapland and comparative samples of non-mineralised Archaean komatiites from the Kovero greenstone belt and Kuhmo greenstone belt, both in eastern Finland, were investigated. The Palaeoproterozoic deposits are represented by the Sakatti Cu-Ni-PGE deposit and Lomalampi PGE-(Ni-Cu) deposit in the Central Lapland greenstone belt. Also, some reference samples for iron oxide trace element measurements were chosen from the other Ni-Cu deposits: Kevitsa (Finland), Pechenga (Russia) and Jinchuan (China). The location of the studied deposits and general information on them are shown in Fig. 6 and Table 2, respectively. Table 2 also shows which research targets were used for isotope and oxide studies. More detailed geological descriptions of the studied deposits can be found from the research articles.

For paper I, samples were collected from 44 drillcores during a research program of the Geological Survey of Finland. For paper II, a total of 40 samples were selected at the Loppi national drillcore archive of the Geological Survey of Finland. Paper III is based on a total of 19 samples collected at the core shed of AA Sakatti Mining Mining Oy's Sodankylä office. Thin and thick sections for

the iron oxide study (paper IV) were prepared using 46 samples collected from drillcores at the Loppi archive and some samples from previous studies and the rock collection of Oulu Mining School, University of Oulu. The Re-Os isotopic analyses reported in Papers II and III were performed totally for 11 whole-rock samples and 81 mineral separates.



**Fig. 6.** Locations of the main research targets (red circles) with some komatiite-hosted deposits and komatiite occurrences. Figure edited from Moilanen et al. (2019) with the permission from publisher.

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	Location	Age	Parental magma	Host rock of mineralisation	Iron oxide occurrence style	Re- Fe- Ds ox	References
Ruossakero Ni-(Cu)	Enontekiö, northern Finland	Archaean	Komatiite (Ti- depleted)	Olivine cumulate	Disseminated magnetite with disseminated sulphides and remobilised Cr-magnetite veins with Ni-sulphides. Magnetite rims in chromite grains.	×	Konnunaho et al. (2015), Konnunaho (2016)
Tulppio Ni- PGE mineralisation	Savukoski, northern Finland	Archaean	Komatiite or komatiitic basalt	Dunite	Cr-magnetite grains and Cr-magnetite and magnetite grains with trace sulphides.	×	Heikura et al. (2009) and Maier et al. (2013)
Vaara Ni-(Cu- PGE)	Kuhmo, eastern Finland	Archaean	Komatiite (Al- undepleted)	Olivine cumulate	Sulphide-magnetite aggregates (oxidation of sulphides), interstitial magnetite (from serpentinisation of silicates), magnetite veins and secondary magnetite rims around chromite grains.	×	Konnunaho et al. (2013), Konnunaho et al. (2015) and Konnunaho (2016)
Hietaharju Ni- (Cu-PGE)	Kuhmo, eastern Finland	Archaean	Komatiitic basalt	Olivine cumulate	Magnetite and Cr-magnetite in massive sulphides, Cr-magnetite with sheared and disseminated sulphides and magnetite rims around chromite grains.	×	Konnunaho et al. (2015), Konnunaho (2016) and Konnunaho et al. (2016)
Tainiovaara Ni-(Cu-PGE)	Lieksa, eastern Finland	Archaean	Komatiite (Al- undepleted)	Olivine cumulate	Magnetite and Cr-magnetite with disseminated sulphides. Magnetite rims around chromite grains.	× ×	Konnunaho et al. (2015) and Konnunaho (2016)
Kovero	Eastern Finland	Archaean	Komatiite	Olivine cumulates with no known mineralisation	Disseminated magnetite, Cr-magnetites after alteration of chromite.	×	Konnunaho (1999)
Lomalampi PGE-(Ni-Cu)	Sodankylä, northern Finland	Palaeoprot.	Komatiitic basalt-low-Mg komatiite (Al- undepleted)	Olivine cumulate	Magnetite and Cr-magnetite with sulphides, dissemination, remobilised magnetite veins and magnetite rims around chromites.	×	Konnunaho et al. (2015), Konnunaho (2016) and Törmänen et al. (2016)
Sakatti Cu-Ni- PGE	Sodankylä, northern Finland	Palaeoprot.	Komatiite- picrite	Olivine cumulate	Trace element composition of magnetite was not studied in this study	×	Brownscombe (2016), Brownscombe et al. (2015)
Kevitsa Ni- Cu-PGE	Sodankylä, northern Finland	Palaeoprot.	Picrite-basalt	Olivine pyroxenite	Magnetite and Cr-magnetite with disseminated sulphides.	×	Mutanen (1997), Yang et al. (2013), Santaguida et al. (2015) and Luolavirta et al. (2017)
Pechenga Ni- Cu-(PGE)	Northwest Russia	Palaeoprot.	Ferropicrite	Gabbro- wehrlite	Magnetite and Cr-magnetite in massive sulphides and disseminated magnetite and sulphide.	×	Hanski (1992) and Hanski et al. (2011)
Jinchuan Ni- Cu-PGE	Northwest China	Neoprot.	High-Mg basalt	Dunite- Iherzolite	Magnetite with remobilised and sheared textured disseminated sulphides.	×	Chai and Naldrett (1992) and Yang et al. (2018)

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#### **7 REVIEW OF ORIGINAL PUBLICATIONS**

#### 7.1 Paper I

Törmänen, T., Konnunaho, J.P., Hanski, E., Moilanen, M., Heikura, P., 2016. The Paleoproterozoic komatiite-hosted PGE mineralization at Lomalampi, Central Lapland Greenstone Belt, northern Finland. *Mineralium Deposita* 51, 411–430.

Paper I concerns the komatiite-related Lomalampi PGE-(Ni-Cu) deposit, which is located in the Central Lapland Greenstone Belt in northern Finland. The deposit is associated with a peridotite cumulate body. Magmatic sulphides (pentlandite, pyrrhotite, chalcopyrite) in the deposit occur as disseminated-type, low-grade mineralisation with the following whole-rock compositions: S 0.4-2 wt.%, Ni <0.5 wt.%, Cu <0.4 wt.%, total PGE > 500 ppb. Palladium minerals are located within silicates and sulphides and only one platinum-bearing mineral, sperrylite, is mainly hosted by silicates. This paper focuses on petrological and geochemical features of the komatiitic rocks in the area and chalcophile element and sulphur isotope characteristics of the deposit.

The main conclusions of this paper are the following:

I) Komatiitic rocks of the Lomalampi deposit are part of the Palaeoproterozoic magmatism of the Central Lapland and are associated with sulphur-bearing sedimentary rocks (black schists) of the Matarakoski Formation.

II) The composition of parental magma to the Lomalampi deposit is low-Mg komatiite or komatiitic basalt, which was enriched in PGE.

III) The mineralisation is composed of a pyrrhotite-chalcopyrite-pentlandite sulphide mineral assemblage, representing a magmatic low-grade disseminated PGE-(Ni-Cu) type II deposit. It is sulphur and base metal poor (S 0.4–2 wt. %, Ni <0.5 wt.% and Cu <0.4 wt.%) and relatively enriched in PGE (Pt + Pd >500 ppb), resulting in exceptionally high PGE/(Ni+Cu) (Fig. 7). IV)  $\delta^{34}$ S shows positive values (+10 to +15‰), differing clearly from the mantle values (0 ± 2 ‰) and indicating contamination with footwall black schist material.

V) The Pt/Pd ratio of ~2.2 is anomalous, clearly exceeding the values in common komatiitic Ni-Cu-PGE deposits world-wide (Pt/Pd around ~0.5) (Fig. 7). This is possibly related to mantle melting processes or/and a regional-scale Pt/Pd heterogeneity in the mantle.



**Figure 7.** Pd/(Ni+Cu) vs. Pt/(Ni+Cu) diagram for the Lomalampi PGE-(Ni-Cu) deposit and komatiite-hosted Ni-Cu deposits worldwide (data from Naldrett, 2004).

#### 7.2 Paper II

Moilanen, M., Hanski, E., Konnunaho, J., Yang, S.-H., Törmänen, T., Li, C., Zhou, L.M., 2019. Re-Os isotope geochemistry of komatiite-hosted Ni-Cu-PGE deposits in Finland. *Ore Geology Reviews* 105, 102–122.

Paper II deals with the Re-Os isotope systematics of Finnish komatiite-hosted Ni-Cu-PGE deposits, including the Archaean Ruossakero Ni-(Cu), Vaara Ni-(Cu-PGE), Tainiovaara Ni-(Cu-PGE) deposits and the Ni-PGE sulphide mineralisation related to a dunitic body at Tulppio, and the Palaeoproterozoic Lomalampi PGE-(Ni-Cu) deposit. Previously, Re-Os isotopes from these komatiitic deposits have not been determined and main purpose of this study was to make age estimations and determine petrogenetic indicators for these deposits with Re-Os isotopes.

The major conclusions from this study are the following:

I) The Lomalampi PGE-(Ni-Cu) deposit yields a Re-Os isochron age of  $2058 \pm 93$  Ma (Fig. 8A), linking the deposit to the ca. 2.05–2.06 Ga mafic-ultramafic magmatism of the Central Lapland greenstone belt, which represents an important ore-formation episode including the Kevitsa Ni-Cu-PGE ore deposit ( $2058 \pm 4$  Ma; Mutanen and Huhma, 2001) and potentially the Sakatti Cu-Ni-PGE deposit (Moilanen et al., 2021). The komatiites of the Savukoski Formation ( $2056 \pm 25$  Ma; Hanski et al., 2001b) also belong to this event. After submitting the papers of this dissertation,

Puchtel at al. (2020) published similar Re-Os and Sm-Nd ages of  $2049 \pm 13$  Ma and  $2046 \pm 22$  Ma, respectively, for these komatiites.

II) The new Re-Os age estimates for the Archaean komatiitic deposits (Fig. 8), Ruossakero (2990  $\pm$  750 Ma), Vaara (2719  $\pm$  140 Ma) and Tainiovaara (2753  $\pm$  47 Ma), are consistent with the previous indirect age determinations. It was also confirmed that the mineralised Tulppio Dunite is Archaean in age (T<sub>RD</sub> model age of 2680  $\pm$  88 Ma).

III) Most of the Os isotopic compositions of Os-rich (> 10 ppb) chromites from the studied Archaean and Palaeoproterozoic Ni-Cu deposits have near-chondritic initial  $\gamma$ Os values (Fig. 9), indicating that Os is derived mostly from a mantle source with a chondritic Re-Os isotope evolution and contamination with radiogenic Os is not reflected in the Os isotope signatures of chromites.

IV) In contrast, chromites from mineralised olivine cumulates of the Lomalampi PGE-(Ni-Cu) and Tainiovaara Ni-(Cu-PGE) deposits have moderately high  $\gamma$ Os values of  $+24 \pm 18$  and  $+13 \pm 1$  (Fig. 9), respectively, indicating some amount of contamination with radiogenic Os. A potential contaminant in the Lomalampi deposit is country rock black schist, which is also supported by strong sulphur isotope evidence (Paper IV). The source of contamination in the Tainiovaara case is unclear, as no proper Os-bearing sources are known to occur in the neighbourhood of the Tainiovaara deposit.

V) Sulphides from the Palaeproterozoic Lomalampi deposit show slightly positive (Fig. 10) or also negative  $\gamma$ Os values, which are interpreted as resulting from of minor/moderate contamination with radiogenic crustal material and disturbance of the Os isotopic system, respectively. The  $\gamma$ Os values of sulphide samples from Archaean komatilitic deposits are near chondritic (Fig. 10).

VI) Osmium isotopic compositions of disseminated sulphides and sulphide-bearing black schists from the Lomalampi area and sulphides from the Vaara deposits show resetting of the isotopic system at ca. 1.85 Ga (Fig. 11), indicating that both magmatic and sedimentary sulphides were widely reset during the Svecofennian orogeny in the Archaean basement and the Palaeoproterozoic supracrustal belts in northern and eastern Finland.



**Fig. 8.** Re-Os isochrons for Finnish komatiite-hosted Ni-Cu-PGE deposits. Disturbed samples are presented as open symbols and are not included in the isochron calculations. Figure is from Moilanen et al. (2019).



**Fig. 9.** Os (ppb) against initial  $\gamma$ Os for chromite separates from komatiitic deposits. Figure is from Moilanen et al. (2019).



**Fig. 10.** Os (ppb) against initial  $\gamma$ Os values for bulk-sulphide samples from the studied komatiitic deposits and wholerock black schist (contaminants for the Lomalampi mineralisation) samples from the country rocks of the Lomalampi deposit. The black schist samples marked with S contains abundant sulphides. Figure taken from Moilanen et al. (2019).



**Fig. 11.** A) Re-Os isochron diagram for samples from the Lomalampi PGE-(Ni-Cu) deposit with 2.05 Ga (dashed) and 1.85 Ga reference lines (initial <sup>187</sup>Os/<sup>188</sup>Os = 0.584). B) Re-Os isochron for the Vaara Ni-(Cu-PGE) deposit with 2.82 Ga (dashed) and 1.85 Ga reference lines (initial <sup>187</sup>Os/<sup>188</sup>Os = 0.1321). Figure is taken from Moilanen et al. (2019).

#### 7.3 Paper III

Moilanen, M., Hanski, E., Yang, SH., 2021. Re-Os isotope geochemistry of the Palaeoproterozoic Sakatti Cu-Ni-PGE sulphide deposit in northern Finland. *Ore Geology Reviews*, 132.

Paper III deals with the Re-Os isotope geochemistry of the Palaeoproterozoic Sakatti Cu-Ni-PGE sulphide deposit, which is located in the Central Lapland greenstone belt in the northern Finland. The deposit includes three mineralised olivine cumulate units (main, north-east and south-west bodies). The sulphide mineral assemblage is typical for magmatic sulphide deposits, including

pyrrhotite, pentlandite, chalcopyrite, and also locally abundant pyrite and magnetite. Sulphides form massive, semi-massive, disseminated and vein-type (stockwork) ores in ultramafic host rocks. The main objective of the paper was to provide constrains on the timing of ore formation and post-magmatic alteration processes, and also determine the initial Os composition of minerals. In addition, reasons for sulphide saturation were discussed.

The key findings from this study are the following:

I) Using whole-rock, olivine, chromite, different sulphide mineral and magnetite separate samples, a Re-Os isochrone age of  $2063 \pm 35$  Ma (Fig. 12a) and a T<sub>MA</sub> model age of 2050 Ma +40/-39 Ma (Fig. 12c) were obtained. This Palaeoproterozoic age is in agreement with the age of the previously dated mafic-ultramafic magmatism of the Savukoski Group in the Central Lapland greenstone belt (CLGB), including komatiitic and picritic volcanism (Sm-Nd isochron age  $2056 \pm 25$  Ma; Hanski et al., 2001b), the Kevitsa Ni-Cu-PGE sulphide ore deposit (U-Pb zircon age of  $2058 \pm 4$  Ma; Mutanen and Huhma, 2001) and the Lomalampi PGE-(Ni-Cu) sulphide mineralisation (Re-Os isochron age of  $2058 \pm 93$  Ma; Moilanen et al., 2019). The geochronological information obtained for the Sakatti deposit connects it to this important ore-forming event of the CLGB.

II) Osmium in the parental magma to the Sakatti deposit is mostly derived from a mantle source, as indicated by most of the chromite and olivine separates and whole-rock samples from olivine cumulates of the Sakatti main body which yielded close-to-zero  $\gamma$ Os(2058 Ma) values.

III) Sulphide and magnetite separates give moderately radiogenic isotope compositions ( $\gamma$ Os from +21 to +56) suggestive of a minor/moderate degree of contamination with crustal material. Chromite separates have chondritic  $\gamma$ Os values whereas sulphide separates have supra-chrondritic values. This suggests that sulphur saturation took place mainly after the chromite grains crystallised from the magma. One potential reason for the isotopic difference is that the location of the sulphide saturation was distal to the Sakatti magma chamber, with the injection of sulphur-saturated magma into the chamber taking place after the onset of chromite crystallisation.

IV) Geochemical features of the Sakatti deposit are similar to those of the Kevitsa deposit, including relatively high Cu/Ni in the sulphide phase, moderately heavy sulphur (Grinenko et al., 2003; Brownscombe et al., 2015) and similar radiogenic Os isotope compositions of sulphides ( $\gamma$ Os averages +33) for Sakatti massive sulphide samples and  $\gamma$ Os is around +20 for the Kevitsa main ore type (Hanski et al., 1997), and strongly negative  $\epsilon$ Nd(2060 Ma) values in ultramafic cumulates (from -2.8 to -6.0 at Sakatti, Brownscombe, 2016; from -2.9 to -6.5 at Kevitsa, Huhma et al., 2018). This is clear evidence for crustal contamination both in the Sakatti and Kevitsa deposits.

V) Sulphide separates from massive sulphide samples yield variable Re-Os errorchron ages ranging from  $1852 \pm 200$  Ma to  $2045 \pm 300$  Ma, and all samples together yield a Re-Os isochron age of  $1928 \pm 16$  Ma (Fig. 13). This indicates an open-system behaviour in sulphide samples, with resetting of sulphides likely having taken place during the Svecofennian orogeny.



**Fig. 12.** Re-Os isochrons for samples from the Sakatti Cu-Ni-PGE deposit. A) Re-Os isochron for selected (n = 30) whole-rock samples and chromite, olivine, sulphide and magnetite separates. B) Re-Os isochron diagram for least altered chromite, olivine and whole-rock samples (8 chromites, 1 olivine, 3 whole-rock samples). C) Weighted-average  $T_{MA}$  model ages for least altered chromite, olivine and whole-rock samples. The black thick line represents the median value of the data set. The same data as in Fig. 12B. Initial  $\gamma$ Os calculated with the age of 2058 Ma. Figure is from Moilanen et al. (2021).



**Fig. 13.** A) Re-Os isochrons for all massive sulphide samples (A) and individual samples (B-H) from the Sakatti Cu-Ni-PGE deposit. A) All compiled sulphide and magnetite separates. B) Spotted-textured pyrite-pyrrhotite-dominant massive sulphide sample from the SW satellite body. The sample texture shows a relatively high degree of alteration and therefore the youngest Re-Os errorchron age. C) Pyrite-chalcopyrite-pyrrhotite-dominated massive sulphide sample. D) Chalcopyrite-dominated massive sulphide sample. E) Pyrrhotite-pentlandite dominated massive sulphide sample. F) Chalcopyrite-pyrrhotite-dominated massive sulphide sample. H) Pyrrhotite-pentlandite-chalcopyrite-dominated massive sulphide sample. F) Chalcopyrite-dominated massive sulphide sample. F) Chalcopyrite-chalcopyrite-dominated massive sulphide sample. H) Pyrrhotite-pentlandite-chalcopyrite-dominated massive sulphide sample. F) Chalcopyrite-chalcopyrite-dominated massive sulphide sample. F) Chalcopyrite-chal

#### 7.4 Paper IV

Moilanen, M., Hanski, E., Konnunaho, J., Törmänen, T., Yang, S.-H., Lahaye, Y., O'Brien, H., Illikainen, J., 2020. Composition of iron oxides in Archean and Paleoproterozoic mafic-ultramafic hosted Ni-Cu-PGE deposits in northern Fennoscandia: application to mineral exploration. *Mineralium Deposita* 55, 1515–1534.

Paper IV focuses on iron oxide compositions in Archaean and Palaeoproterozoic mafic-ultramafic Ni-Cu-PGE deposits. The main research targets were the Archaean Ruossakero Ni-(Cu), Hietaharju, Vaara and Tainiovaara Ni-(Cu-PGE) deposits, the Tulppio dunite and Ni-PGE mineralisation, and the Palaeoproterozoic Lomalampi PGE-(Ni-Cu) deposit. In addition, the Pechenga (Russia), Jinchuan (China) and Kevitsa Ni-Cu-PGE sulphide deposits (Finland), and barren komatiites in the Kovero area (Finland) were studied. These deposits have various magmatic and post-magmatic histories, providing good change to analyse the composition of iron oxides which were formed from different parental magma compositions and equilibrated under different geological conditions. This provides also an opportunity to test iron oxide compositions as a tool applied to mineral exploration.

The main findings in this paper are the following:

I) Magnetite compositions in massive sulphide samples can vary from Cr-magnetite to magnetite.

II) The trace element concentrations of oxide phases differ by 2–3 orders of magnitude, being a reflection of the silicate and sulphide melt compositions from which they have crystallised. Also, post-magmatic modification has affected the compositions. The latter process is manifested by high concentrations of Ni, Cu and Pb in magnetite grains (e.g., magnetite from the Vaara deposit).

III) Average nickel concentration in the oxide phase is a function of the average Ni tenor (in 100% sulphide fraction) of the host rock as indicated by the positive correlation in Fig. 14. The same phenomenon is observed both for magmatic and post-magmatic magnetite generations. The Ni concentration in iron oxide can be a primary magmatic feature or a result of the formation of secondary magnetite via post-magmatic oxidation of sulphides.

IV) Magnesium is lowest in magnetite grains from massive sulphide samples (Hietaharju and Pechenga). This could be a diagnostic feature of the composition of an oxide phase crystallised together with MSS (Fe-rich) in a microenvironment which was more or less isolated from the associated silicate magma/liquid.



**Fig. 14.** Ni tenor vs. Ni concentration in magnetite. Based on LA-ICP-MS data from Moilanen et al. (2020) and literature. Abbreviations of deposits: HIE = Hietaharju; JIN = Jinchuan; KEV = Kevitsa; LAC = Lac des Iles; LOM = Lomalampi; NOR-TAL = Noril'sk-Talnakh; PEC = Pechenga; RAG = Raglan; RUO = Ruossakero; SUD = Sudbury; TUL = Tulppio; VAA = Vaara. Other data sources for magnetite concentration and Ni tenor data: Mutanen, 1997; Osmond et al., 2002; Naldrett, 2004 and references therein; Yang et al., 2013; Boutroy et al., 2014; Konnunaho et al., 2015; Duran et al., 2016; Djon et al., 2018. Figure from Moilanen et al. (2020).

V) Magnetite compositions (e.g., high Ni, low Mg, high Ga in magnetites from massive sulphides samples), different discrimination diagrams (Fig. 15) and sulphide inclusions in magnetite (Fig. 16) could be potentially used as an exploration tool for Ni-Cu-PGE deposits, especially in glaciated terrains (e.g., Fennoscandia), but more studies are required especially from non-mineralised rocks to get more comprehensive dataset for discrimination between mineralised and non-mineralised samples.



**Fig. 15.** Discrimination diagrams for magnetites. Based on LA-ICP-MS data. A) Ni/Cr vs. Ti diagram (Dare et al., 2014). B) Cr/V vs. Ni diagram (Ward et al., 2018). C) Si + Mg vs. Ni + Cr diagram (Dupuis and Beaudoin, 2011). D) Ga + Co vs. Ge diagram (Liu et al., 2015). Figure is taken from Moilanen et al. (2020).



**Fig. 16.** BSE images of sulphide inclusions in magnetite. A) Rounded pyrrhotite-pentlandite sulphide inclusion in magnetite in a massive sulphide sample, Hietaharju deposit. B) Sulphide-magnetite grain aggregate, Vaara deposit. The sulphide grains enclosed by magnetite are not inclusions sensu stricto, but sulphide grains formed by oxidation of previous magmatic sulphides. C) Rounded pyrrhotite-pentlandite inclusions with magnetite, Lomalampi deposit. D) Pentlandite inclusions in magnetites and Cr-magnetites, Tulppio mineralisation. E) and F) Sulphide inclusions in magnetite from a massive sulphide sample, Pechenga deposit. CPY = chalcopyrite, Cr-MGT = Cr-magnetite, MGT =magnetite, MIL = millerite, PN = pentlandite, PO = pyrrhotite, PY= pyrite. Figure from Moilanen et al. (2020).

#### **8 DISCUSSION AND CONCLUSIONS**

The main aim of this PhD study was to collect new mineralogical, chemical and isotope data from Archaean and Palaeoproterozoic Ni-Cu-PGE deposits to get a better understanding of the processes that lead to the formation of the deposits and develop potential new methods for mineral exploration. One goal was to obtain new geochronological and initial Os isotope compositions for mineralised and non-mineralised mafic to ultramafic intrusions and lava flows. The Re-Os system was applied to several Archaean Ni-Cu-(PGE) deposits, including Ruossakero, Vaara, and Tainiovaara, and a low-grade Ni-(PGE) mineralisation at Tulppio. Comparative samples of non-mineralised Archaean komatiites from the Kovero greenstone belt and Kuhmo greenstone belt were investigated. Isotope compositions were also measured for samples from two Palaeoproterozoic deposits, the Sakatti Cu-Ni-PGE deposit, and Lomalampi PGE-(Ni-Cu) deposit.

Besides isotopic investigations, in-situ major and trace element compositions of iron oxides from sulphide ores and associated ultramafic rocks were determined to get new mineral chemical data and test whether iron oxide compositions could be used as an exploration tool. Trace element compositions of iron oxides were studied from the following Archaean Ni-Cu-(PGE) deposits:

Ruossakero, Hietaharju, Vaara and Tulppio dunite with a low-grade Ni-(PGE) mineralisation and Palaeoproterozoic Lomalampi PGE-(Ni-Cu) deposit. Also, some reference samples were analysed from the Pechenga (Russia), Jinchuan (China), and Kevitsa (Finland) Ni-Cu-PGE sulphide deposits, and a barren komatiite sequence in the Kovero area (Finland).

Suitable mineral separates for the Re-Os isotopic geochronology and petrogenetic indicator studies are chromite, olivine from ultramafic cumulate rocks and if there are sulphides available, different sulphide separates can also be used for Re-Os geochronological studies.

The Re-Os isotopic system provides an important tool for getting geochronological and genetic information from Ni-Cu-PGE deposits related to mafic-ultramafic rocks. Especially from massive sulphide samples, in which Re and Os are most likely equilibrated in sulphide minerals and there is a good possibility to determine geologically meaningful magmatic Re-Os ages. It may be difficult to obtain reliable estimates of initial Os isotopic compositions using disseminated sulphide samples because Os diffusion between sulphides are inhibited by silicates between sulphides and consequently, equilibrium was not reached in disseminated samples (Yang et al., 2008). Compared to the U-Pb method, the Re-Os method is less precise but can still provide useful age information. In some cases, Re-Os ages are close to and even more precise than the ages determined by the Sm-Nd method. For example, Puchtel et al. (2020) showed that whole-rock samples and olivine and chromite separates from komatilitic rocks in Finnish Central Lapland define a Re-Os isochron age of 2049  $\pm$  13 Ma while whole-rock and clinopyroxene separate samples yield an identical Sm-Nd isochron age of  $2046 \pm 22$  Ma. Our case studies showed that ages for magmatic Ni-Cu-PGE deposits could be determined with the Re-Os method, especially when using a large number of samples and mineral separates from different genetically related rock types (e.g., the Sakatti case in this study). In this research, we got a Re-Os isochron age of  $2063 \pm 35$  Ma for the Sakatti Cu-Ni-PGE deposit and a Re-Os isochron age of  $2058 \pm 93$  Ma for the Lomalampi PGE-(Ni-Cu) deposit. These ages connect these deposits to the ca. 2.05-2.06 Ga mafic-ultramafic magmatism, which is an important event in terms of formation of magmatic Ni-Cu-PGE deposits in the CLGB. Also, the Kevitsa Ni-Cu-PGE deposit dated at 2058  $\pm$  4 Ma (Mutanen and Huhma, 2001), the komatiitic rocks of the Jeesiörova area and the komatiitic dykes cutting the Kevitsa intrusion belong to the same magmatic event (Hanski et al., 2001b; Puchtel et al., 2020). Other mafic-ultramafic intrusions in the CLGB dated by the U-Pb zircon method close to this magmatic event are Moskuvaara (2039  $\pm$  14 Ma), Satovaara (2025  $\pm$  8 Ma), Puijärvi (2035  $\pm$  8 Ma), and Rovasvaara (2055  $\pm$  5 Ma) (Huhma et al., 2018). Komatiites with a similar age also occur in the northern Norway, in the Karasjoki greenstone belt, where they have yielded a wholerock Sm-Nd age of  $2085 \pm 85$  Ma (Krill et al., 1985) and a recent U-Pb zircon age of  $2051 \pm 8$  Ma (Orvik et al., 2022).

Some chromite samples from the Lomalampi and Tainiovaara deposits have radiogenic Os isotopic compositions indicating some amount of contamination with crustal material. Also, bulk-sulphide samples from Lomalampi and sulphide and magnetite separates from Sakatti show radiogenic Os compositions, which is suggestive of a minor/moderate degree of contamination with crustal material. This is an important piece of information as introduction of external radiogenetic Os to magmas from sulphur-bearing crustal rocks (e.g., black shales and/or anhydrites) increases the S concentration of the magma and leads in favourite cases to sulphur saturation and formation of a magmatic sulphide deposit.

In summary, the above-mentioned observations show that the Re-Os isotopic system is a powerful research tool together with other dating methods for studying the geochronology of magmatic Ni-Cu-PGE deposits, and chromite and sulphide separates offer a unique opportunity to determine the origin of Os and, by inference, other PGE in these deposits. In the future, more of these deposits could be dated and their Os source determined with the Re-Os isotope system, and this would deepen our understanding of the magmatic evolution of northern Fennoscandia.

Because of the magnetite structure can incorporate a large range of trace element components depending on geological formation conditions and available elements, this makes magnetite a useful mineral in exploration or studying the genesis of different types of ore deposits (e.g., Carew et al., 2006; Singoyi et al., 2006; Dupuis and Beaudoin, 2011; Dare et al., 2012; 2014; Galicki et al., 2012; Boutroy et al., 2014; Maia et al., 2022; Nadoll et al., 2014; Huang et al., 2014; Duran et al., 2016; Makvandi et al., 2016; Ward et al., 2018; Makvandi et al., 2021). For example, Dare et al. (2012), Boutroy et al. (2014), Dupuis and Beaudoin (2011), and Duran et al. (2016) have used magnetite compositions to discriminate potential magmatic Ni-Cu-PGE deposits.

As was shown by the study iron oxide compositions, magnetite provides a potential tool for exploration of magmatic Ni-Cu-PGE deposits in glaciated terrains, but still a more comprehensive dataset of oxide compositions is needed, especially from mineralised and non-mineralised ultramafic rock units. One suggestion for future studies would be a heavy-mineral till sampling line across a known magmatic Ni-Cu-PGE deposit and analysis of magnetite grains from till heavy mineral fraction to test whether there are signatures of mineralisation in magnetite compositions or Ni-bearing sulphide or PGE inclusions in magnetite. Also, it is important to study how many oxide grain analyses per till sample are needed to get a statistically reliable amount of data. Recently, prediction-based machine learning models have been developed using magnetite trace

element compositional data to predict occurrences of ore deposits (Bédard et al., 2022). They used magnetite data from Moilanen (2020) to test their machine learning (random forest algorithm) model and predicted that almost 61% of the observations were correctly identified to belong to Ni-Cu-PGE deposits. Machine learning model could be developed especially for Fennoscandian Ni-Cu-PGE deposits when more data are available from different types of deposits.

Some important questions for future research have appeared during this study. One could be the comparison between initial Os isotope compositions ( $\gamma$ Os) of chromite from olivine cumulate samples and in-situ concentrations of Cu and other trace elements in olivine (cf. Locmelis et al., 2019) in the same samples. This could give information on the timing of sulphide saturation or whether it has occurred at all. Another future study could focus on iron oxide compositions from massive sulphide samples, assessing how common Cr-magnetite is in these samples. An important research question is also how to discriminate between primary magmatic magnetite from secondary hydrothermal magnetite. This discrimination is important when studying magmatic magnetite, which can give information on original magmatic processes. To refine the Ni tenor vs. Ni in oxide diagram (Fig. 14), a more detailed study would be needed using individual samples for which both the Ni tenor and Ni concentration in the oxide phase have been determined, and not just average compositions for different deposits as was done in this study. Also, information on olivine compositions could be compared with oxide compositions, as the Ni tenors of Ni-Cu-PGE deposits are also positively correlated with olivine Ni contents (e.g., Naldrett, 2004; Lamberg, 2005). This kind of study would also give important information on the extent of the partitioning of nickel between primary and secondary silicates, oxides and sulphides during magmatic and metamorphic processes. In future studies, it would also be interesting to look in more detail at the Ni content of the secondary silicates (serpentine, chlorite) that have equilibrated with Ni-rich sulphides.

The following conclusions can be made from this research.

1) The obtained Re-Os isochrons yield the following ages: Sakatti  $2063 \pm 35$  Ma, Lomalampi 2058  $\pm 93$  Ma, Vaara  $2719 \pm 140$  Ma, and Tainiovaara  $2753 \pm 47$  Ma. The age of  $2990 \pm 750$  Ma calculated For the Ruossakero deposit a highly imprecise, and the Tulppio T<sub>RD</sub> model age of 2680  $\pm 88$  Ma (implying minimum age) is compatible with its assumed Archaean age. As can be seen from the relatively large errors in these ages, the Re-Os system has its limitations and usually needs other age determination methods to confirm the ages. Nevertheless, the obtained Re-Os isochron ages are in agreement with previous age determinations from these deposits or their geological constraints.

**2**) Chromites and sulphides from the studied deposits have different Os isotope characteristics. Most of the studied chromite separates both from the Archaean and Palaeoproterozoic Ni-Cu deposits show near-chondritic initial Os isotope compositions, indicating that Os is mostly derived from a mantle source with a chondritic Re-Os isotope evolution. In contrast, most of the sulphide samples from the two Palaeoproterozoic Ni-Cu deposits have radiogenic Os compositions. This indicates that in most cases, contamination with radiogenic material during ore formation is not reflected in the Os isotope composition of chromite. One explanation could be that they crystallised before the magma reached sulphide saturation.

**3)** Two chromite separates from mineralised olivine cumulates of the Lomalampi and Tainiovaara Ni-(Cu-PGE) deposits show moderately high  $\gamma$ Os values of  $+24 \pm 18$  and  $+13 \pm 1$ , respectively, indicating some amount of contamination with radiogenic Os. In the case of the Lomalampi deposit, potential contaminants are country rock black schists, which is also supported by strong sulphur isotope evidence (Paper IV) and highly radiogenic Os isotope compositions of sulphides in black schists. The contaminant at Tainiovaara is unknown; no appropriate Os-bearing sources are known to occur in the vicinity of the deposit.

4) Sulphide and magnetite separates from the Sakatti deposit show radiogenic Os isotope compositions, with the average initial  $\gamma$ Os values varying between +21 and +56. This suggests a minor/moderate degree of contamination with crustal material. The chondritic and suprachondritic  $\gamma$ Os values for chromite and sulphide separates, respectively, imply that sulphur saturation took place after chromite crystallisation.

**5**) The Sakatti deposit shares several geochemical features with the Kevitsa deposit, including relatively high Cu/Ni in the sulphide phase, moderately heavy sulphur isotope compositions, similar radiogenic Os isotope compositions of sulphides, and strongly negative  $\epsilon$ Nd(2060 Ma) values in ultramafic cumulates. This indicates that both these deposits share a similar petrogenetic history and potentially belong to the same magmatic stage in the evolution of the Central Lapland greenstone belt.

6) Rhenium-osmium isotope compositions of some sulphides from the Sakatti, Vaara and Lomalampi deposits and sulphide-bearing black schists from the Lomalampi area indicate resetting of the Os isotopic system at ca. 1.85-1.90 Ga (Figs. 11 and 13). Sulphide separates from massive sulphide samples from Sakatti have varying Re-Os errorchron ages ranging from  $1852 \pm 200$  Ma to  $2045 \pm 300$  Ma, with all samples pooled together yielding a Re-Os isochron age of 1928  $\pm 16$  Ma. These observations indicate that both magmatic and sedimentary sulphides were broadly

reset during the Svecofennian orogeny affecting both the Archaean basement and the Palaeoproterozoic supracrustal cover in northern and eastern Finland.

**7**) Trace element abundances of oxide phase differ from 2 to 3 orders of magnitude as a reflection of the silicate and sulphide melt compositions from which they have crystallised.

8) Oxides in massive sulphide samples can vary from Cr-magnetite to magnetite.

**9)** The average Ni concentration in magnetite is a function of the average Ni tenor (in 100% sulphide fraction) of the host sulphide ore. This concerns both primary magnetite and magnetite produced by post-magmatic hydrothermal processes.

**10**) Magnetite grains in massive sulphide samples from the Hietaharju and Pechenga deposits have the lowest Mg concentrations among the studied samples. This could be a diagnostic feature of an oxide phase that crystallised together with MSS (Fe-rich) in a microenvironment which was more or less isolated from the associated silicate magma.

**11**) By combining petrographical observations (especially Ni-bearing sulphide inclusions inside magnetite, see Fig. 16), oxide phase compositions (e.g., high Ni, low Mg, high Ga in magnetites from massive sulphides, high Ni in high Ni tenor deposits), and different discrimination diagrams (Fig. 15), all this information could be potentially used as an exploration tool. Especially in glaciated terrains (e.g., Fennoscandia), heavy mineral separates (e.g., chromite and/or magnetite) from till samples could be studied with this method. However, the method has its limitations, and more studies are required especially from non-mineralised rocks to get more comprehensive dataset and improve the quality of discrimination between mineralised and non-mineralised rocks.

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