Bachelor of Science

in

Geology

A TIDALLY RESEDIMENTED ESTUARINE MUDFLAT ORIGIN FOR THE SURFICIALLY NI-ZN-CU-CO –ENRICHED PALEOPROTEROZOIC TALVIVAARA FORMATION, FINLAND

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Tiivistelmä/Referat – Abstract

The Paleoproterozoic metasedimentary Talvivaara formation (ca. 2.1–1.95 Ga) in Sotkamo, Finland, hosts one of the largest sulfidic nickel resources in Europe (2053 Mt ore; Ni 4.5 Mt, Zn 10.3 Mt). Globally, the Talvivaara ore deposit is the largest shale-hosted Ni-(Cu-PGE) sulfide mineralization in production. This work summarizes the preliminary results of ongoing revised ore-genetic studies by Geological Survey of Finland (GTK), which contradict the current prevailing model relating the poly-metallic Ni-Zn-Cu-Co –enrichment of the Talvivaara fm "black shales" to presumed hydrothermal activity in a stratified, restricted rift basin.

Sedimentology and geochemistry of drill core DDKS-010 (length 476.40 m) from the Kolmisoppi ore-body was studied in detail, also additional trace element and high-resolution isotopic data has been obtained. The drill core intersection from 476.40 m to ca. 390 m forms stratigraphically nearly continuous well preserved succession, which has allowed integrated sedimentological studies that have not been previously viable. The new results indicate a synsedimentary, paleomarine hydrogenous metal enrichment for the Talvivaara fm carbonaceous sulfide-rich mudstones–siltstones, and the sediments are interpreted to have been mainly tidally resedimented into deeper water proximal offshore environment in a narrow intracratonic seaway from a nearby estuarine mudflat.

Avainsanat – Nyckelord – Keywords

Talvivaara, Kolmisoppi, Sulfidic sedimentary rocks, Iron-rich sediments, Black shale, Nickel, Zinc, Paleo-oceanography, Mudstones, Tidal environments, Precambrian sedimentology

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Sotkamon paleoproterotsooisen Talvivaara-muodostuman Ni-Zn-Cu-Co –rikastuminen estuaaristen mutatasannesedimenttien tidaalisen uudelleenkerrostumisen kautta

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Tiivistelmä/Referat – Abstract

Paleoproterotsooisista metasedimenttikivistä koostuva Sotkamon Talvivaara-muodostuma (n. 2.1–1.95 Ga) sisältää erään Euroopan suurimmista sulfidisen nikkelin varannoista (2053 Mt malmia; Ni 4.5 Mt, Zn 10.3 Mt). Globaalisti vertailtuna Talvivaaran malmiesiintymä on maailman suurin tuotannossa oleva hienorakeisten sedimenttikivien isännöimä Ni-(Cu-PGE) mineralisaatio. Tässä työssä annetaan lyhyt yhteenveto Geologian tutkimuskeskuksen (GTK) uusien malmigeneettisten tutkimusten alustavista tuloksista. Malmigeneettinen uudelleenarviointi tulee muuttamaan tällä hetkellä vallitsevaa aiempaa mallia, jossa Talvivaara-muodostuman ”mustaliuskeiden” monimetallinen Ni-Zn-Cu-Co –rikastuminen on yhdistetty oletettuun hydrotermiseen aktiivisuuteen kierroltaan rajoittuneessa, kerrostuneessa merellisessä repeämäaltaassa.

Kolmisopen malmion kairasydämen DDKS-010 (pituus 476.40 m) sedimentologia ja geokemia on paraikaa yksityiskohtaisten tutkimusten kohteena; myös täydentävää hivenalkuaineanalytiikkaa sekä korkean resoluution isotooppidataa on jo hankittu. Syvyydellä 476.40–390 m kairasydän DDKS-010 lävistää lähes yhtenäisen hyvin säilyneen stratigrafisen seurannon, mikä on mahdollistanut integroidut sedimentologiset tutkimukset jollaisia alueella ei ole aiemmin voitu toteuttaa. Uudet tulokset viittaavat Talvivaara-muodostuman hiilipitoisten sulfidirikkaiden mutakivien–silttikivien paleomariiniseen, hydrogeeniseen metallirikastumiseen, ja sedimenttien tulkitaan kerrostuneen uudelleen pääasiassa vuorovesiprosessien johdosta syvempään rannikon tuntuman proksimaaliseen meriympäristöön (kapeassa intrakratonisessa merikäytävässä) läheisen jokisuiston mutatasanteelta.

Avainsanat – Nyckelord – Keywords

Talvivaara, Kolmisoppi, Sulfidiset sedimenttikivet, Rautarikkaat sedimentit, ”Mustaliuskeet”, Nikkeli, Sinkki, Paleomerigeologia, Mutakivet, Vuorovesiympäristöt, Prekambrin sedimentologia

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CONTENTS

PREFACE

This Bachelor of Science thesis is a preliminary overview briefly summarizing the main results and conclusions of the more comprehensive M.Sc. studies by the present author (Laitala, *in prep.*). This B.Sc. thesis is based on a poster presentation by Laitala and Lahtinen (2014), held at the Geological Society of America Annual Meeting in Vancouver, B.C., Canada, on October 20, 2014. As the poster presentation represents the equally shared intellectual contributions by both of the authors but was entirely studied, written and carried out by the first author, this thesis formalizes the sole responsibility of the present author for the interpretational, written, pictorial, and layout content of the aforementioned presentation.

1. Introduction: Talvivaara ore deposit – Europe's largest Ni-project

The Talvivaara ore deposit is located ca. 25 km from Sotkamo, eastern Finland (Figure 1). The polymetallic Talvivaara ore deposit (Ni-Zn-Cu-Co-U) is comprised of Kuusilampi and Kolmisoppi orebodies, which together contain ca. 2053 Mt ore @ 4.5 Mt Ni and 10.3 Mt Zn (Talvivaara Plc. 2012, 2014), constituting one of the largest nickel resources in Europe (USGS 2013). The relatively low-grade but large tonnage sulfide ore is being utilized by using bacterially catalyzed bioheapleaching (Riekkola-Vanhanen 2013). Nickel deliveries started in 2009, and when in full-scale production, the mine is aiming at 50 000 t / year level (Talvivaara Plc. 2014). The Talvivaara ore deposit is currently genetically classified as SEDEX (Loukola-Ruskeeniemi and Heino 1996; Goodfellow and Lydon 2007), and as recently as in 2014, Mudd and Jowitt (2014) included it in the category of hydrothermal Ni-deposits. Jowitt and Keays (2011, p. 194) review the hydrothermal genetic model proposed by Loukola-Ruskeeniemi and Heino (1996), but consider also the syngenetic, hydrogenous seawater-scavenging model proposed by Kontinen et al. (2006). Globally, the metamorphically upgraded Talvivaara ore deposit is the largest shale-hosted Ni-(Cu-PGE) sulfide mineralization currently in production (Jowitt and Keays 2011).

2. Geologic setting

2.1. Regional geology

The polymetallic Talvivaara ore deposit is hosted by the Paleoproterozoic C-S-Fe –rich Talvivaara formation, which belongs to the Sotkamo group (ca. 2.06–1.96 Ga) of primarily metasedimentary Kainuu Belt (Fig. 1). Overview on the geology of the Kainuu Belt is provided by Laajoki (2005). The ca. 200-km-long Kainuu Belt overlies a reactivated Neoarchean suture zone between Archean blocks (Kontinen et al. 2007; Lentua and Rautavaara Complexes in Fig. 1). Rifting of the Archean Karelian craton margin at ca. 2.22–2.1 Ga and opening of the Svecofennian paleosea at 2.1 Ga on the western side of the Rautavaara Complex led to extensional deepening of the Kainuu basin (Korja et al. 2006; Lahtinen et al. 2008). The initial block faulting phase included chaotic sedimentation in the lower Sotkamo group (Gehör and Havola 1988), and mafic tuffite interbeds in ca. 2.1 Ga clastic shallow-water carbonates at Melalahti, Paltamo (60 km NNW of Talvivaara), indicate local magmatism during the incipient rifting stage (Kärki 1988, p. 163). Epiclastic, compositionally Fe-tholeiitic amphibolite schist interbeds occur also in silicate-facies iron formation units of the Tuomivaara and Tenetti formations (ca. 30 km NNE of Talvivaara), which belong lithostratigraphically to the lower or middle part of the Sotkamo group (Gehör and Havola 1988).

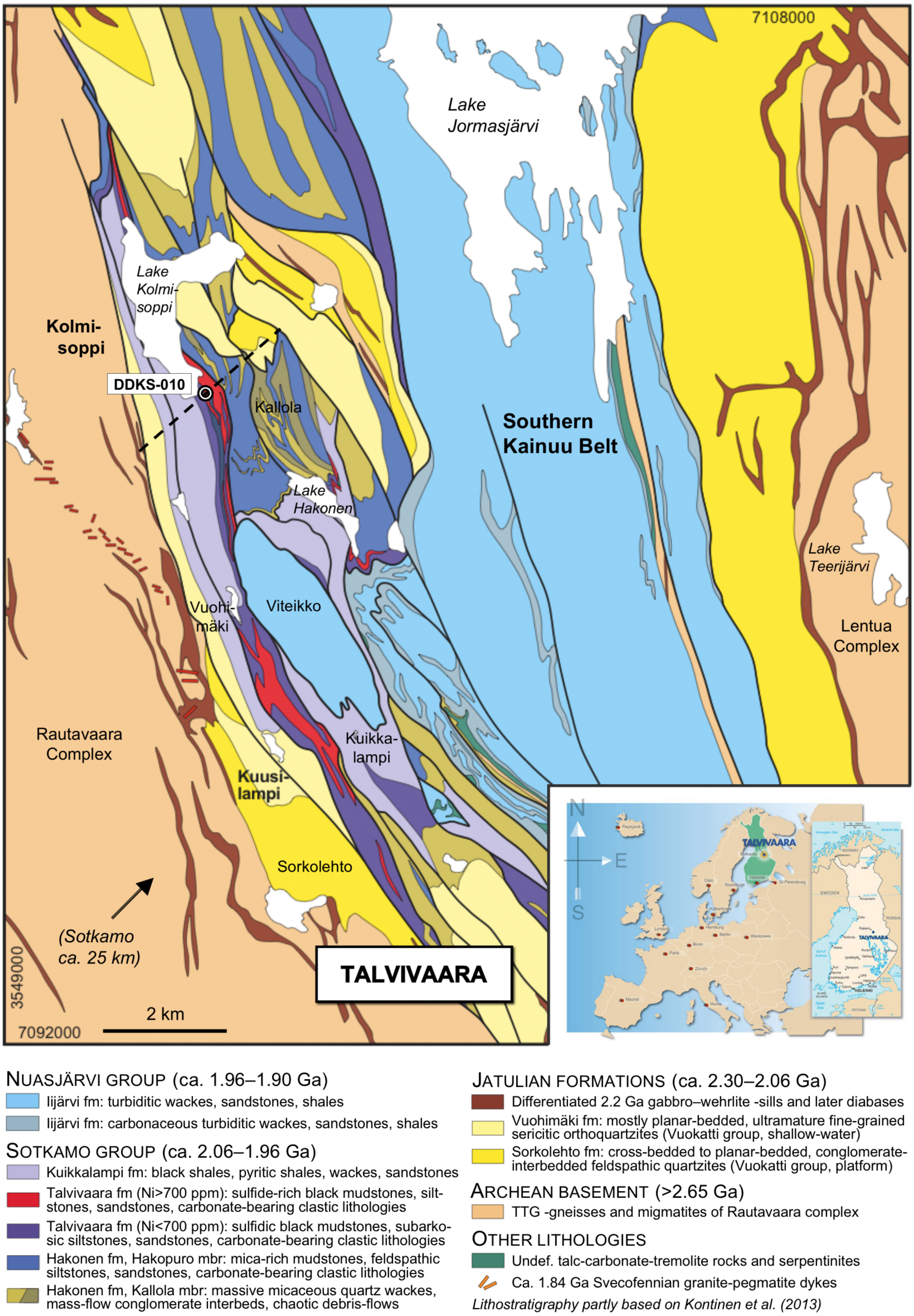

FIGURE 1. Geology of the Talvivaara area, map modified from Kontinen (2012). Sedimentary lithologies in the map legend should be prefixed with "meta-". Small insert map: www.talvivaara.com

The Paleoproterozoic evolution of supracrustal sequences in nearby Russian Karelia has recently been synthesized by Melezhik et al. (2013), and the chronostratigraphic division by Hanski and Melezhik (2013) for the Fennoscandian Shield is broadly followed here (see also Strand et al. 2010). Lower lithostratigraphic age for the Sotkamo group is tentatively correlated here with the end of the Jatulian system (2.30–2.06 Ga) that includes the Great Oxidation Event (GOE) and the related global Lomagundi–Jatuli $\delta^{13}C$ isotopic excursion recorded by sedimentary carbonates (Karhu 1993; Karhu and Holland 1996). Termination of the Jatulian system is precisely bracketed at 2.058–2.060 Ga (Hanski and Melezhik 2013). The Sotkamo group is assigned here in a chronostratigraphic sense to the Ludicovian system (2.06–1.96 Ga) of Hanski and Melezhik, which is traditionally in Finland referred in lithostratigraphical sense as Lower Kaleva. As the Ludicovian of Russian Karelia includes the type locality for the global Shunga event (worldwide deposition of highly C_{org}-rich sediments; Strauss et al. 2013), it would be practical to harmonize the nomenclature by adopting the Ludicovian system also for Finnish usage. Thus, the Talvivaara formation is here informally correlated broadly with the C_{org}-rich sedimentary rocks of the 2.05–1.98 Ga Zaonega fm in the Russian Karelia (*op. cit.*), and globally e.g. with the ca. 2.08–2.02 Ga black shales of the Francevillian basin, Gabon (Ossa Ossa et al. 2013).

2.2. Lithostratigraphy and metamorphism in the Talvivaara area

Kontinen et al. (2013) have recently described the main lithostratigraphic units[1] in the Talvivaara area, which are summarized in Fig. 1. The C_{org} and sulfide-rich black mudstone–siltstone dominated metalliferous Talvivaara formation (TV fm) is underlain by the micaceous sandstone–siltstone dominated Hakonen fm (HK fm), and Kontinen et al. (2013) view the transition as abruptly gradational. The relation to the non-metal enriched overlying Kuikkalampi fm (KL fm) is similarly considered as abruptly gradational, although yet inconclusively defined. As a departure from Kontinen et al. (2013), the Nuasjärvi group (ca. 1.96–1.90 Ga) is here taken to represent autochthonous–parautochthonous deep-water sedimentary units (Gehör and Havola 1988) that were backthrusted in structural inversion and tectonic stacking of the closing intracratonic marginal basin during the ca. 1.90–1.87 Ga Svecofennian orogeny (Korja et al. 2006; Lahtinen et al. 2008). Local metamorphic peak at 1.88–1.87 Ga is given by U–Pb ages from Talvivaara uraninites (Lecomte et al. 2014). Although regional metamorphism in the Kainuu Belt ranges from amphibolite facies in the west to lower greenschist facies in the east (Laajoki 2005), geobarometry by Törnroos (1982) indicates possible low-pressure domains at Kolmisoppi.

[1] This nomenclature should be understood as ”work in progress”, as the formal status of the Talvivaara fm (and other local units belonging to the Sotkamo group) is currently undefined in the national bedrock database of Finland (FinStrati, DigiKP200; www.gtk.fi). The nomenclature of Kontinen et al. (2013) is used here in informal sense.

2.3. Prevailing hydrothermal ore-genetic model – and recent advances

Since the genetic synthesis paper by Loukola-Ruskeeniemi and Heino (1996), the Talvivaara fm sediments have been mostly referred as hydrothermally Ni-Cu-Zn –enriched S and C_{org}-rich black shales (*sensu lato*) deposited in the deeper part of a stratified, restricted marine rift basin (e.g. Pasava et al. 2003; Jowitt and Keays 2011). High median C_{org} (7.6 wt %) and S (8.2 wt.%) values attest to anoxic/euxinic conditions, and iron sulfide δ^{34}S data have been interpreted as evidencing for both bacterial and thermochemical sulfate reduction (Loukola-Ruskeeniemi and Lahtinen 2013). Recently, Young et al. (2013) have also used anomalous fractionations in δ^{33}S data and Δ^{33}S values as arguing for thermochemical reactions during interaction of sulfate-rich hydrothermal fluids with the Talvivaara muds. Ultramafic rocks (serpentinites) occurring in the area have been considered as the most plausible source for Ni (Loukola-Ruskeeniemi et al. 2013). However, recent studies by Kontinen (2012) have placed tight geological constraints for the hydrothermal model: base metal and trace element ratios in Talvivaara point towards redox-controlled synsedimentary metal enrichment in a well connected marine basin with temporally anomalous seawater Ni, Zn, Cu and Co concentrations. Compositional homogeneity of individual mud beds, varying metal concentrations between adjoining sedimentation units (laminae, beds), and mass-flow features have indicated possible redepositional origin for the metalliferous muds (Kontinen et al. 2013). Similar average metal concentrations in other ca. 20 smaller Talvivaara-type occurrences in eastern Finland also support larger basinal controls (Rasilainen et al. 2013, p. 15–17). Other recent studies of Talvivaara are provided by Törmälehto (2008), Laitala (2014, *in prep.*), Laitala and Lahtinen (2014), and Virtasalo et al. (2014).

3. Materials and methods

3.1. Kolmisoppi drill core DDKS-010, obtaining the material

3.1.1. Selecting drill core DDKS-010

After completing a prioritized campaign at the newly opened Kuusilampi open pit, resource definition drilling programme by Talvivaara Plc. (TVA Plc.) began delineating the dimensions of Kolmisoppi orebody more precisely in 2009 (Talvivaara Plc. 2010). As some of the fresh Kolmisoppi cores showed excellent partial preservation of the TV fm sedimentary lithologies, they were sampled by geologist Asko Kontinen (GTK) in late 2009. These initial studies led to launching a M.Sc. project for the present author in February 2010. Final selection of the core suitable for detailed study was done by (then) Talvivaara Plc. mining geologist Hannu Lahtinen and A. Kontinen.

Despite tight overfolding (Fig. 2) and partial tectonic repetition of lithological units, the Talvivaara fm is preserved relatively intact in the lower parts of DDKS-010, up to depth of ca. 390 m (Fig. 2B). Only very basic structural analysis was included in this study.

3.1.2. Drill core logging and sampling (GTK)

Drill core DDKS-010 was logged, studied and sampled at the Talvivaara core facility in 2010. The core was digitally photographed (Canon PowerShot G9, RAW image format; three overlapping high resolution pictures per box + close ups), measured, and sampled for chemical whole-rock analyses (n=75) and thin sections (n=57). Chemical sampling had been preplanned and targeted by R. Lahtinen (GTK), and A. Kontinen provided specialist assistance in selecting the sample material for petrographic studies.

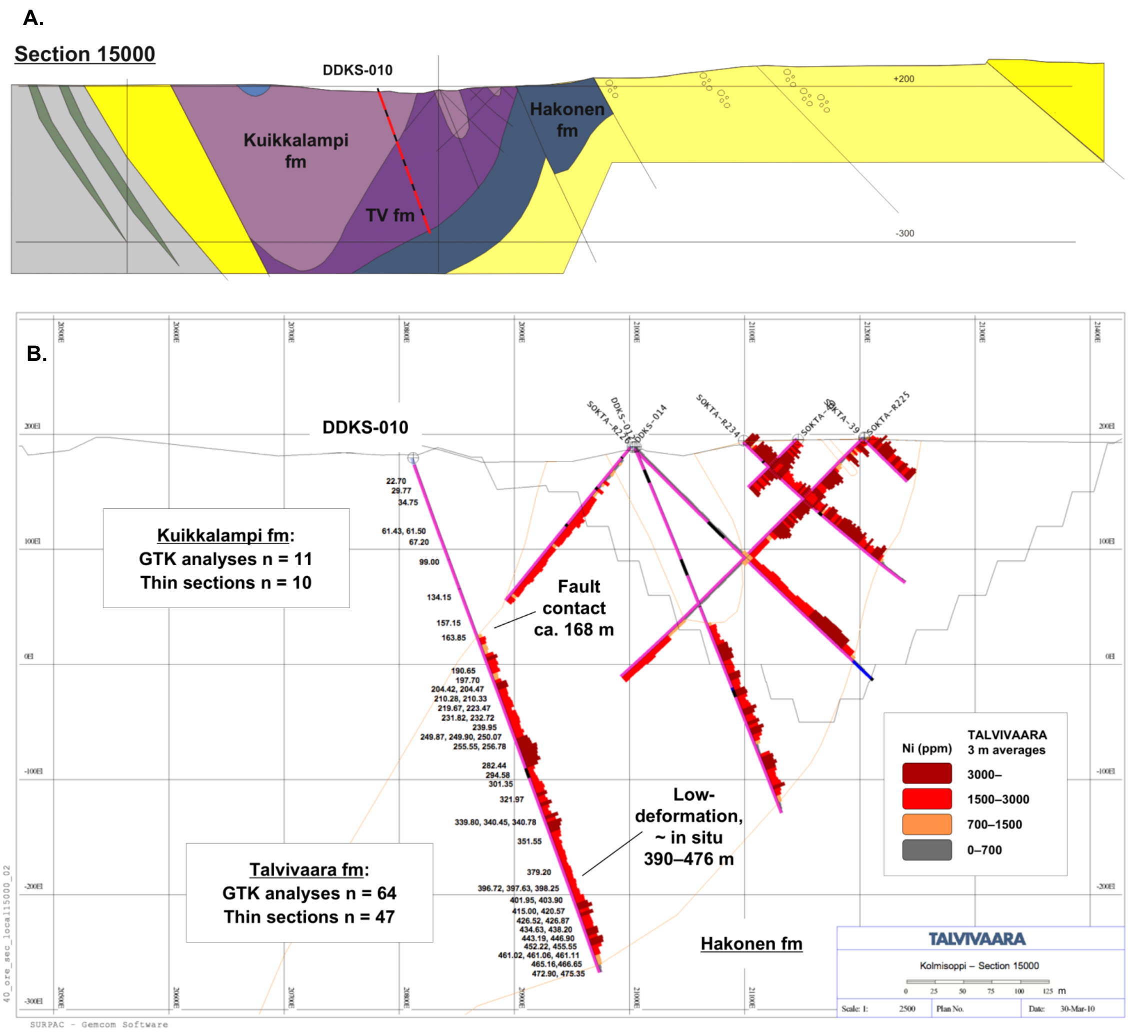

FIGURE 2. A) Geological section of DDKS-010 showing the lithological units of Kolmisoppi drilling profile 15000 (see Fig. 1). Modified from a picture drawn by Asko Kontinen. **B)** SURPAC -section by Talvivaara Mining Co. displaying 3-m average whole-rock Ni-concentrations in drilling holes at Kolmisoppi orebody, section 15000 (as in year 2010). Depths of GTK thin section samples (not resolvable here) are marked on the left side of the DDKS-010 column. Talvivaara Plc. cut-off limit for chemical analyses is <700 ppm Ni in handheld X-ray fluorescence analyzer. Scale bar: 125 m.

3.2. TALVIVAARA PLC., CHEMICAL AVERAGE DATA FROM DDKS-010 (164–476 M)

As an integral part of mineral resource inventorying, deposit scale modeling, and delineation of the Kuusilampi and Kolmisoppi orebodies, Talvivaara Mining Co. Plc. performs chemical whole-rock analyses for longer drill core intersections displaying >700 ppm Ni (cut-off limit for mining) in handheld X-ray fluorescence analyzer. Talvivaara Plc. uses 3-meter sample length for averaging, and the chemically analyzed sections are sampled continuously (further details for the methods used by TVA Plc. are described in Loukola-Ruskeeniemi and Lahtinen 2013). At the initiation of the present study, Talvivaara Plc. mining geologist Hannu Lahtinen provided chemical average data from the analyzed intersection of drill core DDKS-010 (164–476 m; Fig. 2B). Some of the whole-core average data is visualized here in Figs. 3 and 4. The Talvivaara Plc. data proved very useful in preplanning and targeting the detailed GTK sampling.

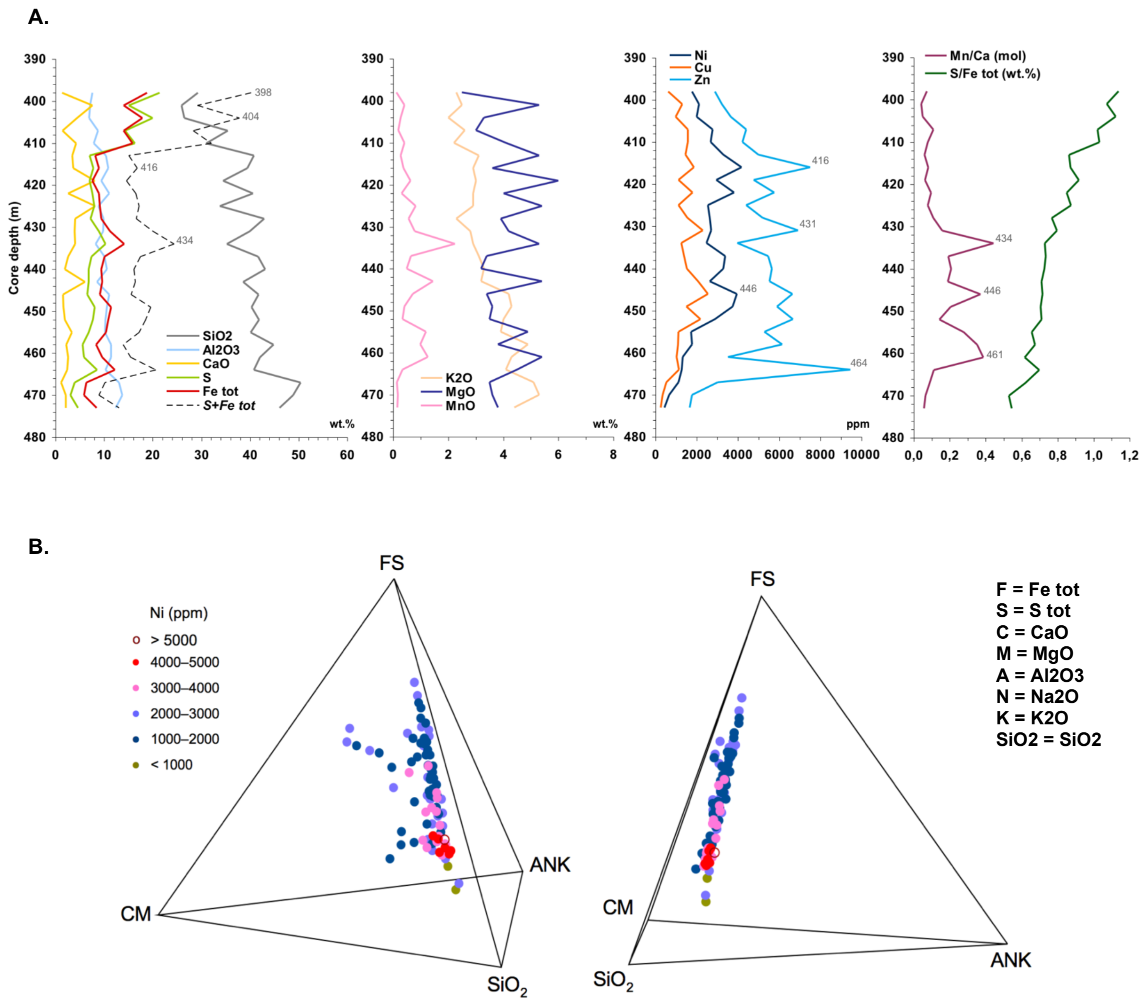

FIGURE 3. A) Chemical profile diagrams between depths 398–476 m showing selected main and minor element average concentrations and ratios in the well-preserved lower part of drill core DDKS-010 (sample length 3 m, data by Talvivaara Plc.). **B)** Main element molar ratio diagram for all TVA Plc. 3-m average analyses (n=104) between depths 164–476 m in DDKS-010. Average Ni levels are shown with color codes.

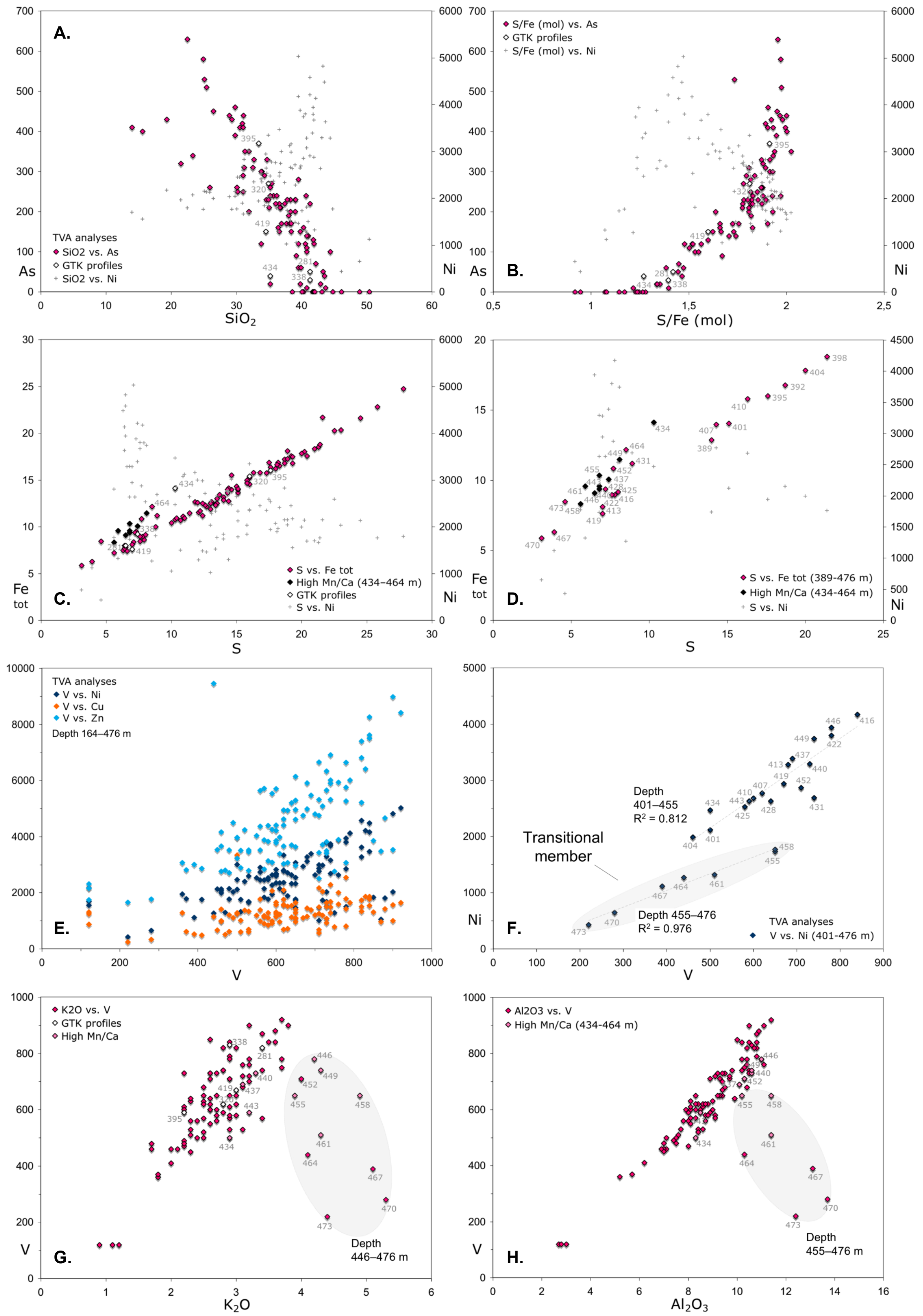

FIGURE 4. Binary and trinary plots from the TVA Plc. average data in DDKS-010 (sample length 3 m, depths 164–476 m, n=104). Depths of GTK profiles are indicated. **A–D)** Diagrams showing the variation in pyrrhotite and pyrite contents. Arsenic (As) is a good proxy for syngenetic pyrite. Lowering of average Ni concentrations with increasing amount of pyrite can be seen in *"S/Fe (mol) vs. As"* and *"S vs. Fe"* diagrams. **E)** Vanadium has good overall linear correlation with Ni, Cu and Zn. **F)** Diagram *"V vs. Ni at depths 401–476 m"* suggests separate original clay-bound and detrital mica-bound vanadium. **G–H)** Upper depth of the transitional siltstone member of Talvivaara fm in drill core DDKS-010 is positioned here at ca. 455 m based on *"K_2O vs. V"* , *"Al_2O_3 vs. V"* and *"V vs. Ni at depths 401–476 m"* (Fig. 4F) diagrams.

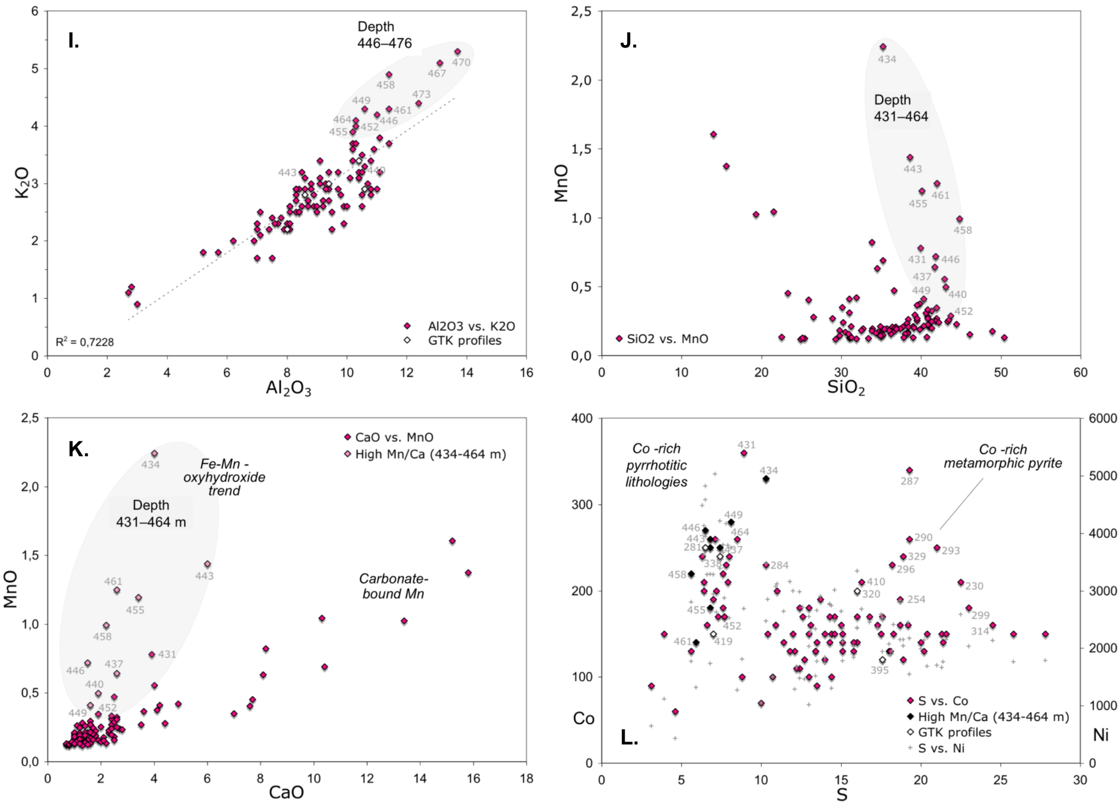

FIGURE 4. *(continued)* **I)** K-feldspathic sand–silt component in the "transitional siltstone member" of TV fm can be seen in higher K/Al ratio at depths 455–476 m. Mica-bound K_2O is high at 455–446 m. **J–K)** *"SiO_2 vs. MnO"* and *"CaO vs. MnO"* diagrams show that besides carbonate-bound MnO, in drill core DDKS-010 there are clearly lithologies with non-carbonate bound Mn (currently in spessartine). High Mn/Ca (molar) ratio is interpreted here to indicate primary lithologies rich in Fe-Mn (oxyhydr)oxides. **L)** *"S vs. Co"*: Cobalt has good correlation with Ni; also separate high-Co trend related to stronger deformation and formation of porphyroblastic high-Co pyrite is seen in drill core depths near the fold hinge zone (at ca. 285–305 m).

3.3. GTK SAMPLES

3.3.1. GTK sample materials and methods

Sampling for this study aimed at representative coverage of the whole drill core DDKS-010, although focusing on the metal-enriched Talvivaara fm (Fig. 2). Lithologies from the Kuikka-lampi fm were sampled for comparison. Total number of chemical samples was 75 (TV fm, n=64; KL fm, n=11), and number of polished thin sections was 57 (TV fm, n=47; KL fm, n=10). Sampling was targeted on visually well-preserved parts but some sections showing minor shearing, silicification and slight mobilization of sulfides were also sampled for controlling secondary effects (Fig. 5). Strongly sheared or obviously altered parts in DDKS-010 were avoided. Six chemical profiles were taken (indicated in Figures 5, 6 and 9 as Profs. 1.–5.; Prof. 6. is grouped in "Mn-rich pyrrhotite mudstones"), plus several additional sample pairs. Chemical whole-rock analyses were performed by Labtium Ltd., Espoo, using XRF and Leco (C_{carb} and C_{org}) –methods. Continuous, good quality drill core box photographs served as sedimentological documentation (Fig. 7). Additional mineralogical (SEM, EPMA) and high-resolution *in situ* iron sulfide Fe and S isotope data (NordSIM, Stockholm; results in preparation) were also obtained, and Virtasalo et al. (2014) performed a separate *in situ* $\delta^{34}S$ and $\delta^{56}Fe$ study on laminated pyrite-rich samples at depth 406.15–406.55 m.

3.3.2. Petrographic studies and present mineralogy of the samples

DDKS-010 thin sections were optically scanned for macroscopic details, then microscoped at transmitted and reflected light (Fig. 8). About thousand microphotographs were taken. Grain-scale isotopic heterogeneities in metaframboidal sedimentary pyrites indicate good preservation of primary signatures despite metamorphic recrystallization. Present main sulfides are pyrite (descriptively subdivided to Py_1–Py_5), pyrrhotite (Po_1–Po_5), sphalerite (Sph), pentlandite, chalcopyrite and alabandite; other mineral phases are quartz, K-feldspar (orthoclase to microcline), phlogopite, biotite, muscovite, plagioclase, carbonate (dolomite to calcite), tremolite, spessartine, rutile, titanite, apatite and thucholite (bitumen-rimmed uraninite grains). Detrital zircon and monazite often display secondary xenotime overgrowths. Pyrite may be completely absent in some lithologies. Carbonaceous matter was petrographically broadly divided into kerogenous (inert restite), bitumenous (mobilated) and graphitic (optically anisotropic) substances.

3.3.3. Sample screening and classification

Inhibitory effect of high C_{org}-content on metamorphic recrystallization of sulfidic black shales was already noted by Peltola (1960). Paleoproterozoic sulfide-rich black metashales (”black schists”) occur widely in Finland, and Kontinen et al. (2006, p. 42) recognized the value of their more detailed lithofacies study. Samples in the present GTK study were screened into chemical alteration categories 1a, 1b, 2 and 3, based on combined elemental coherence, drill core preservation and thin section petrography (Figs. 5–8). Although Bekker et al. (2010, p. 469) downplay the notion of sulfide-facies iron formation, many features observed in DDKS-010 are consistent with the definition of sulfide-facies iron formation *sensu* James (1966). Pyrite-dominated laminated lithofacies forms one sedimentary endmember in Talvivaara fm (Fig. 6A–B), and Laajoki and Saikkonen (1977) have described laminated pyrrhotite-rich units in the broadly contemporary basin-margin iron formations of the Kainuu Belt. High iron-sulfide content and good preservation of the DDKS-010 samples necessitated treating syngenetic–early diagenetic pyrite grains as a sedimentary component (Love and Zimmerman 1961), and a sedimentology-based, semi-quantitative geochemical–petrographical classification scheme was developed for the sulfidic metasedimentary lithofacies applicable to the Talvivaara region (Laitala *in prep.*).

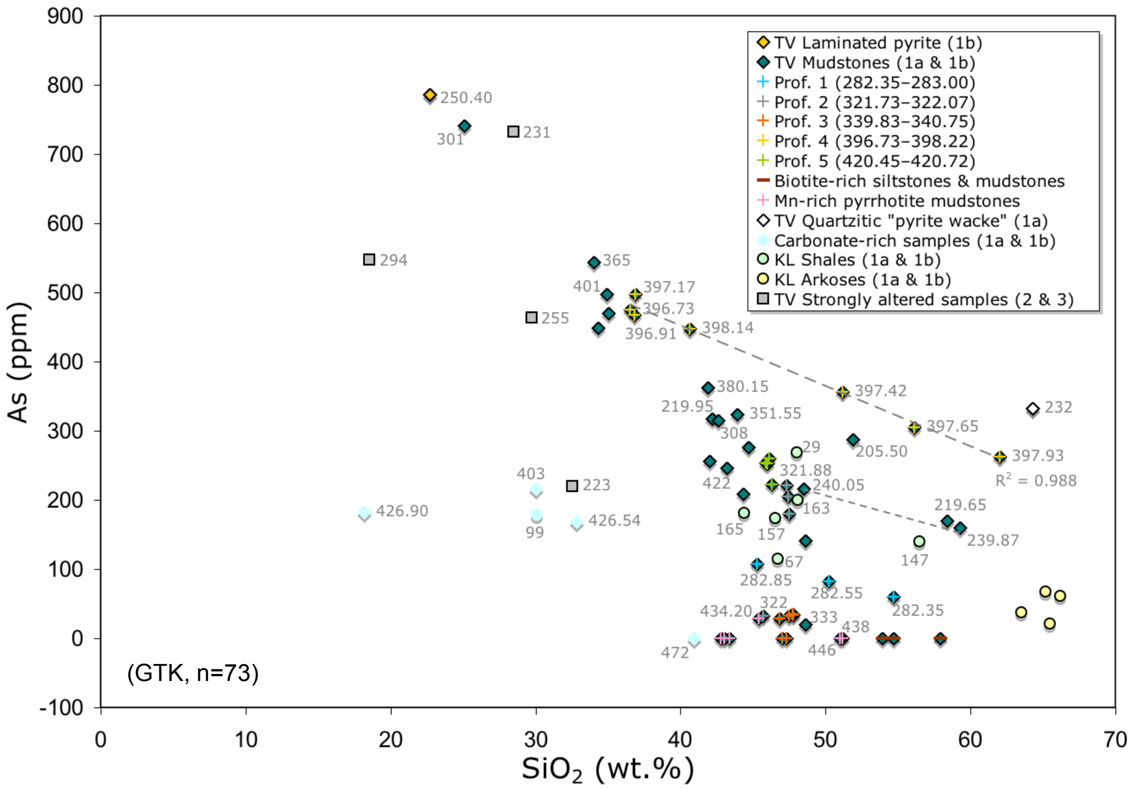

FIGURE 5. SiO_2 vs. As diagram was utilized as part of the screening procedure for GTK samples, which were designated to alteration categories 1a, 1b, 2 and 3. Arsenic (As) is a good proxy for syngenetic–diagenetic pyrite, and sheared 1b samples mainly show only the volumetric dilution by metamorphic silica. Non-altered Cat 1a samples were further used as a basis for more detailed, semi-quantitative chemical–petrographical classification of the sulfidic mudstones, siltstones and shales (claystones) belonging to the Talvivaara and Kuikkalampi formations.

Formation of marine sedimentary sulfides is thoroughly reviewed by Rickard (2012), and it is both conceptually and paleoenvironmentally important to make a distinction to hydrothermally enriched iron sulfide-rich sediments occurring in SEDEX -environments (as described e.g. in Lydon et al. 2000; Goodfellow and Lydon 2007).

4. RESULTS: INTEGRATED SEDIMENTOLOGY, PETROGRAPHY AND GEOCHEMISTRY

4.1. GEOCHEMISTRY OF GTK SAMPLES

Geochemical data and results of the present GTK study will be fully documented in Laitala (*in prep.*), but they are briefly exemplified here with diagrams in Figures 5, 6 and 9. Overall, Ni-Zn-Cu-(Co-Mo) correlate well in the Talvivaara fm (Figs. 6F–G) and follow the increase of clay and C_{org}-rich black sapropel mud component. Scatter in Ni/TOC (Fig. 6E) may partly result from aggregated carbonaceous matter sedimenting also as particular silt-size and larger detrital grains. The observed metal trends agree well with normal paleomarine metal scavenging and redox-controlled processes (e.g. Leventhal 1998). Although manganiferous mudstone lithologies (Figs. 4J–K and Fig. 6A) may indicate proximity to nearby fault-sourced brine fluids (e.g. Large et al. 1998) or volcanic hydrothermal complexes (Lydon et al. 2000), they are also a common feature of shallow oxic environments in redox-stratified marine basins (Force and Cannon 1988; see also Berner 1981). As the formation of sedimentary pyrite is closely dependent on the availability of reactive organic carbon (Berner 1982), dissolved or nanoparticulate reactive iron (Raiswell and Canfield 2012), and bacterially reducible sulfate (Rickard 2012), chemical data in the present study implies a paleoenvironment for Talvivaara formation where all of these conditions were abundantly met.

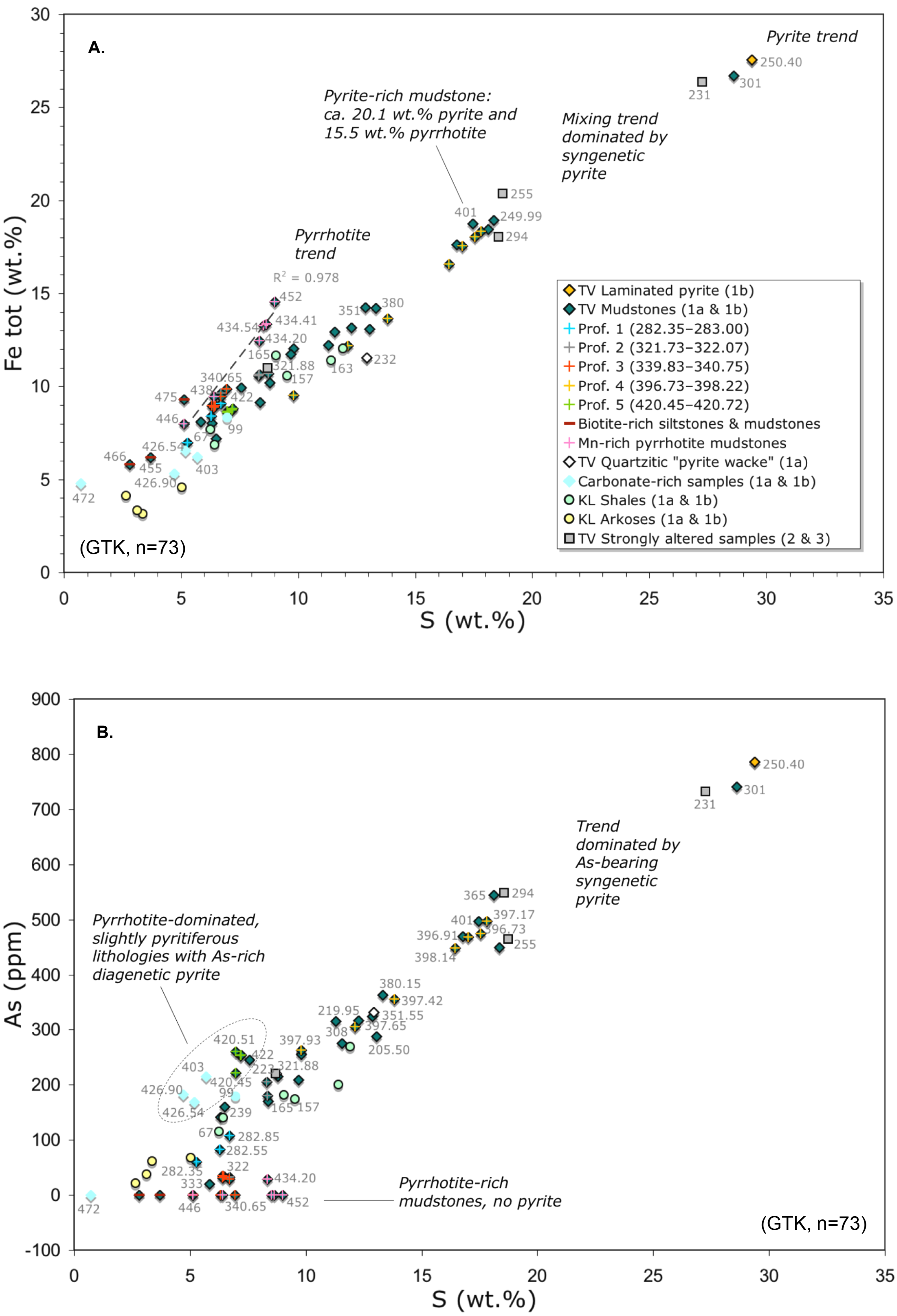

FIGURE 6. A) S vs. Fe $_{tot}$ diagram for the GTK data shows variation in the amounts of iron sulfide components. The distinct separate pyrrhotite trend is interpreted to represent a primary feature related to the precursor sulfides and abundant Fe-Mn (oxyhydr)oxides in the protolith sediments, not as metamorphic pyrrhotitization of pyrite (Laitala and Lahtinen 2014). **B)** Features in S vs. As agree well with thin section observations: high As/S samples occur mostly at depth where minor diagenetic pyrite is first introduced to the sediments.

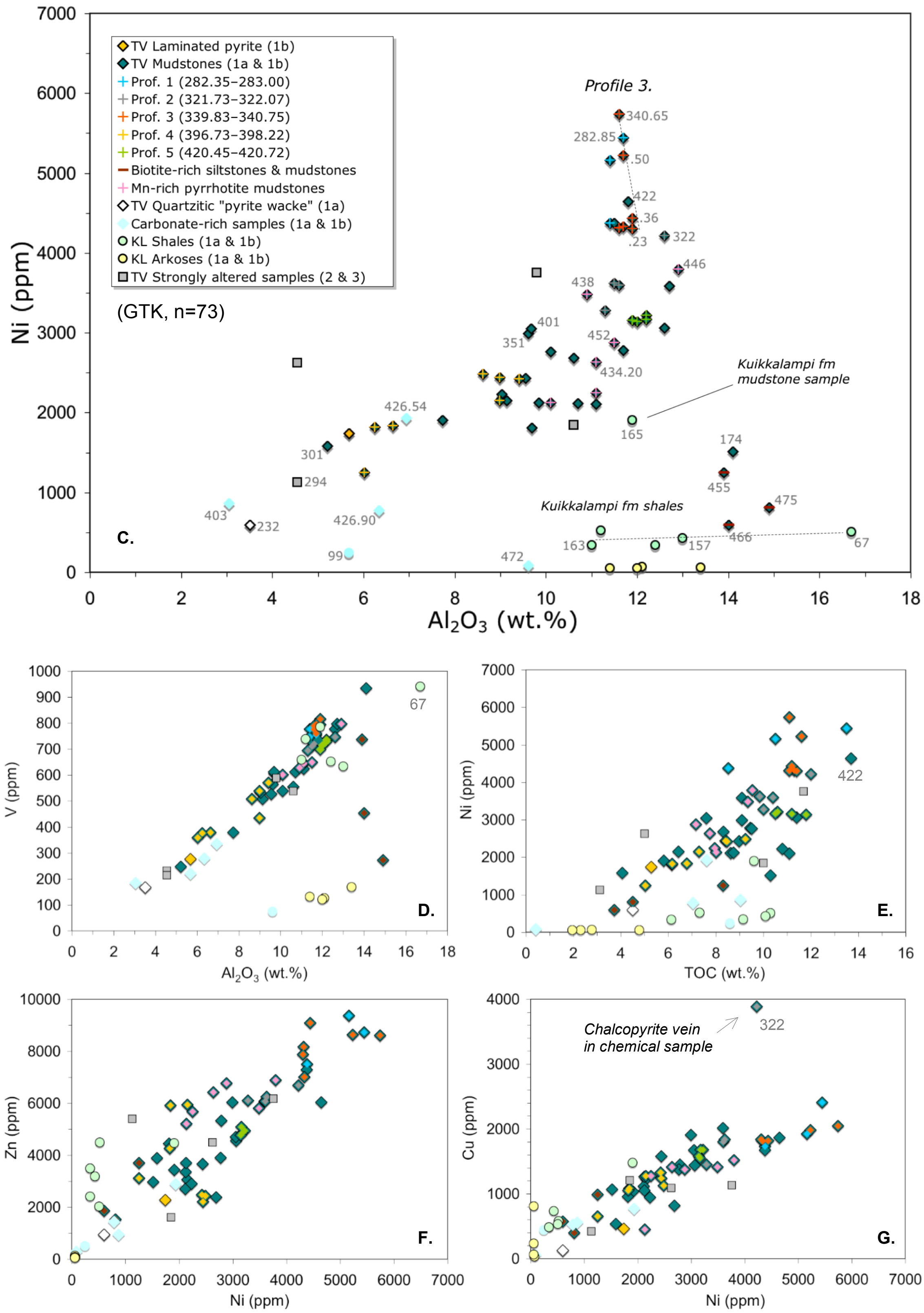

FIGURE 6. (*continued*) **C)** Al_2O_3 vs. Ni shows good overall correlation of Ni with clay-bound Al_2O_3, which is further attributed to clay-C_{org} –association. **D–G)** Simplified diagrams showing some correlations of redox-sensitive elements in GTK data. Al_2O_3 vs. V shows the same overall trend as TVA Plc. average data in Fig. 4H. Broad scatter in TOC vs. Ni may partly result from C_{org} sedimenting as both sapropelic and detrital particular carbonaceous matter. Scatter in Zn/Ni may relate to ready mobilization of sphalerite in more permeable (siltier) mudstones, or primary microbial formation of additional sedimentary sphalerite. Slightly non-linear Ni vs. Cu –trend possibly indicates lower availability of copper in the sedimentary environment.

4.2. Sedimentology, introductory notes

Sedimentology of the drill core DDKS-010 will be treated comprehensively in the forthcoming work (Laitala *in prep.*). The present brief discussion focuses on the stratigraphically nearly continuous low-deformation section between 476.40 m to 390 m. Illustrations are found in Figs. 7–8. Drill core pictures in Fig. 7 are referred by core depths, and thin sections in Fig. 8 by thin section sample depths (e.g. TS 443.19). Overall, this well-preserved metasedimentary sequence is interpreted to represent a deepening, gradational transgressive transition from the underlying non-metal enriched Hakonen fm to the metal-enriched TV fm. The Talvivaara fm is informally divided here into *transitional pyrrhotitic siltstone member* (ca. 476.40–455 m; Figs. 4F–I), *pyrrhotitic mudstone member* (455–431 m), and *pyritiferous mudstone member* (431–390 m). The clastic sedimentary terminology used here broadly follows Potter et al. (2005).

4.3. Transitional siltstone member of Talvivaara fm

The *transitional siltstone member of TV fm* is dominated by subarkosic, partly very biotite-rich, muddy siltstones–fine sandstones and low-Ni black mudstones showing initially graded bedding (Fig. 7; 476.05, 473.29), but transitioning quickly to rhythmic sedimentation displaying diagnostic features of depositional environment with semidiurnal tidal cyclicities (e.g. Williams 2000; Kvale 2012). Thinly mud-draped, horizontally laminated gray silts–fine sands in 470.73 form rhythmically alternating packages with laminated dark silt-rich muds, apparently recording daily to semimonthly or monthly tidal periodicities as detailed by Adkins and Eriksson (1998). Small-scale ripple cross-lamination in TS 466.65 (Fig. 8A) attests also to intermittent dynamic migratory bedform sedimentation of the muddy silts, either from turbidites (Schieber 1990) or waning tidal currents (Jaeger and Nittrouer 1995). Abruptly erosive contact and decrementally fining laminae (from coarse sand to muddy fine sand–silt) in 466.52 may relate to successively weakening ebb-tide current velocities (De Boer et al. 1989). Heterolithic, rhythmically interlaminated graded mica-rich silt/black mud couplets in 461.14 (TS 461.11, Fig. 8A) are a classic feature of vertically accreted tidal rhythmites (Cowan et al. 1998). At 456.05, systematic thickness variations in heterolithic sand–silt/mud couplets seem to record a symmetric, full fortnight (neap–spring–neap) cycle: about 28 semidiurnal lamina couplets (ordinate and subordinate lamina couplets) can be counted, which would indicate deposition of the 20-cm-thick sequence in ca. 14 days (Smith et al. 1990; Figure 6 in Adkins and Eriksson 1998). Upper part of the transitional siltstone member of TV fm is defined here by the increasing dominance of black clay-rich mudstones (455.64; see also Figs. 4F–H), and thin section TS 455.55 (Fig. 8A) appears to retain a plasmic microfabric in horizontally aligned (S_0/S_1) detrital biotite flakes occurring as unistrially concentrated layers (Kuehl et al. 1988; Allison et al. 1995).

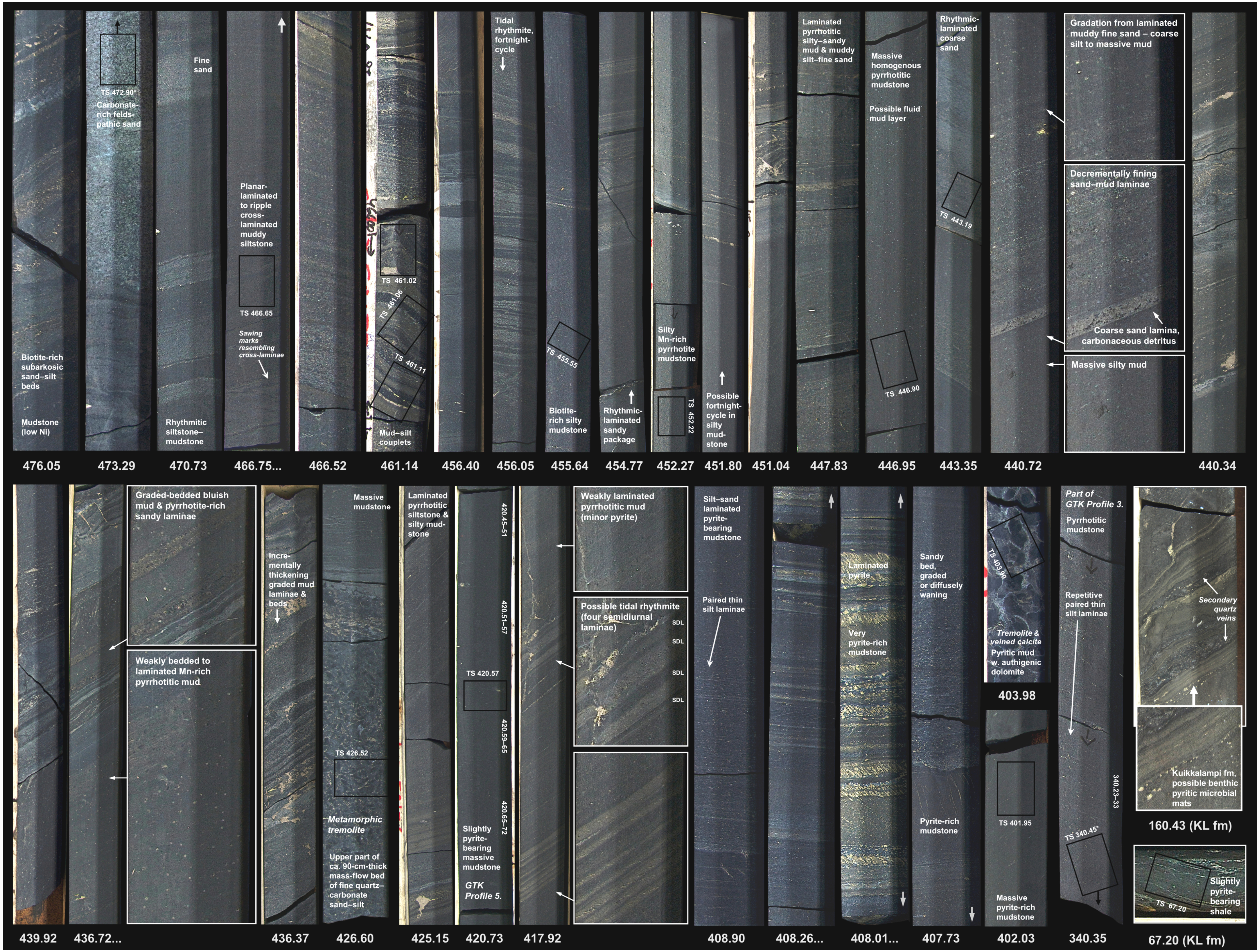

FIGURE 7.

Drill core pictures. Representative lithologies in the stratigraphically nearly continuous well-preserved lower part of DDKS-010.

Talvivaara fm is divided here informally into "transitional pyrrhotitic siltstone member" (ca. 476.40–455 m), "pyrrhotitic mudstone member" (455–431 m) and "pyritiferous mudstone member" (431–390 m). Picture 340.35 shows part of the GTK profile 3., which has the highest systematic Ni-trends of the studied samples. Drill core pictures of Kuikkalampi fm pyritic shales (claystones; 160.43) and slightly pyritic black shales *sensu stricto* (67.20) are shown at lower right.

Scale of the pictures varies, but core diameter is 4 cm. Part of the drill core box is shown for color and brightness reference in some images.

Approximate positions of GTK thin section samples are also marked. Note: drill core depths below the images are only close estimates serving as picture identifiers, not precise measured depths. However, the depths of chemical analyses and thin section samples are exact, as they were measured during sampling.

See the main text for sedimentological explanations.

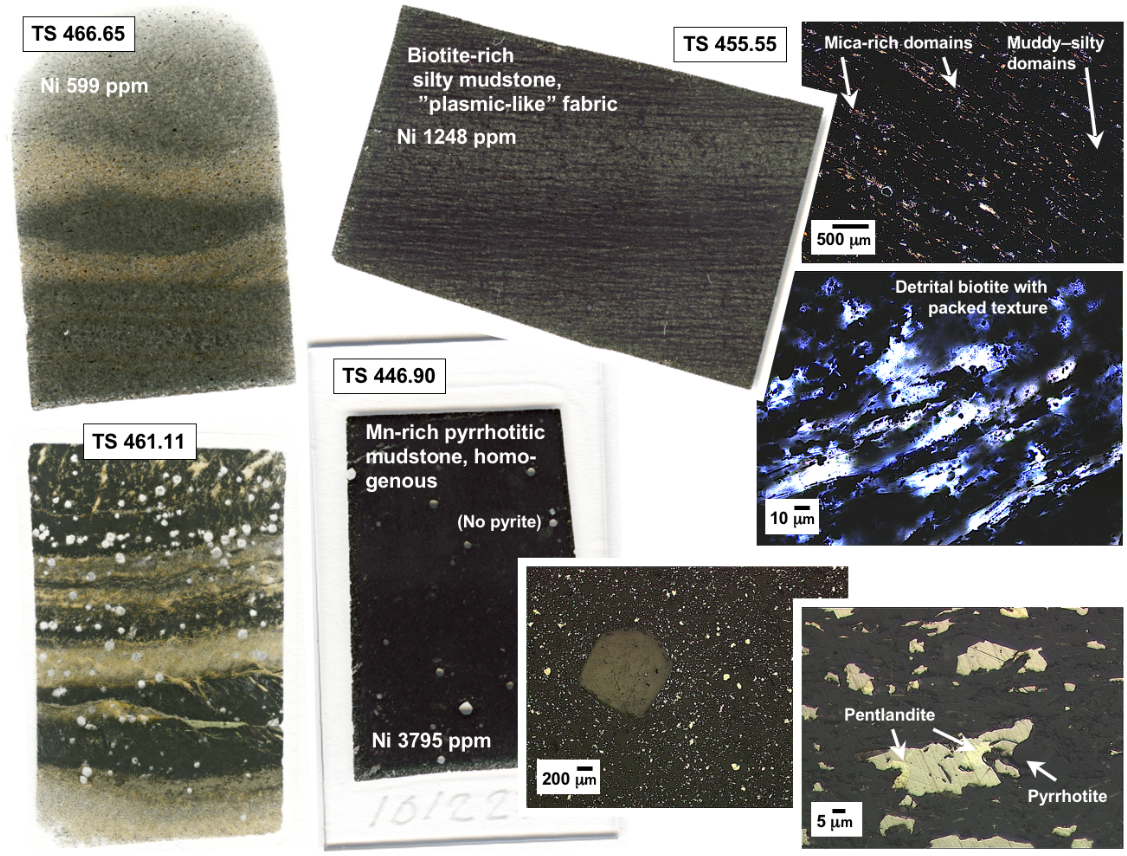

FIGURE 8. A) Thin sections TS 466.65, TS 461.11 and TS 455.55 exemplify the transitional pyrrhotitic siltstone member of Talvivaara fm. Thin section TS 446.90 represents the pyrrhotitic mudstone member of Talvivaara fm, having significantly higher C_{org}-rich sapropelic component and metal concentrations.

4.4. Pyrrhotitic mudstone member of Talvivaara fm

The *pyrrhotitic mudstone member of TV fm* (454.77 to 436.37 in Fig. 7) is dominated by black, fine, clay-rich mudstones having higher sapropelic C_{org}-component and significantly elevated metal concentrations. Frequently occurring rhythmically laminated sandy packages (e.g. 454.77, 451.04, 443.35, 440.34, 439.92) continue to interlude the mud deposition repeatedly; recurring intervals vary from decimeters to meters, apparently recording periodicities from monthly to annual to pluriannual lunar cycles, and seasonal changes in paleotidal range (Williams 2000). In many cases, the sandy packages display similar overall tripartite rhythmicity as in the lower part of image 470.73. Depositional features of the TV fm pyrrhotitic mudstones are illustrated in the drill core pictures (Fig. 7), but completely massive homogenous thick mud layers (as in 446.95) possibly represent deposition from mobilized fluid muds (Jaeger and Nittrouer 1988; Mackay and Dalrymple 2011). Carbonaceous detritus in interluding, rhythmically laminated package of ”microconglomeratic” coarse sand in TS 443.19 (Fig. 8B) has been interpreted as eroded from a nearby siliciclastic intertidal flat (Laitala 2014; see e.g. Tice and Lowe 2006; Schopf 2012). Dynamic, rapid deposition also for the metal-rich muds can be inferred from relatively thick, graded-laminated to bedded Mn and pyrrhotite-rich muds in 436.72–436.37.

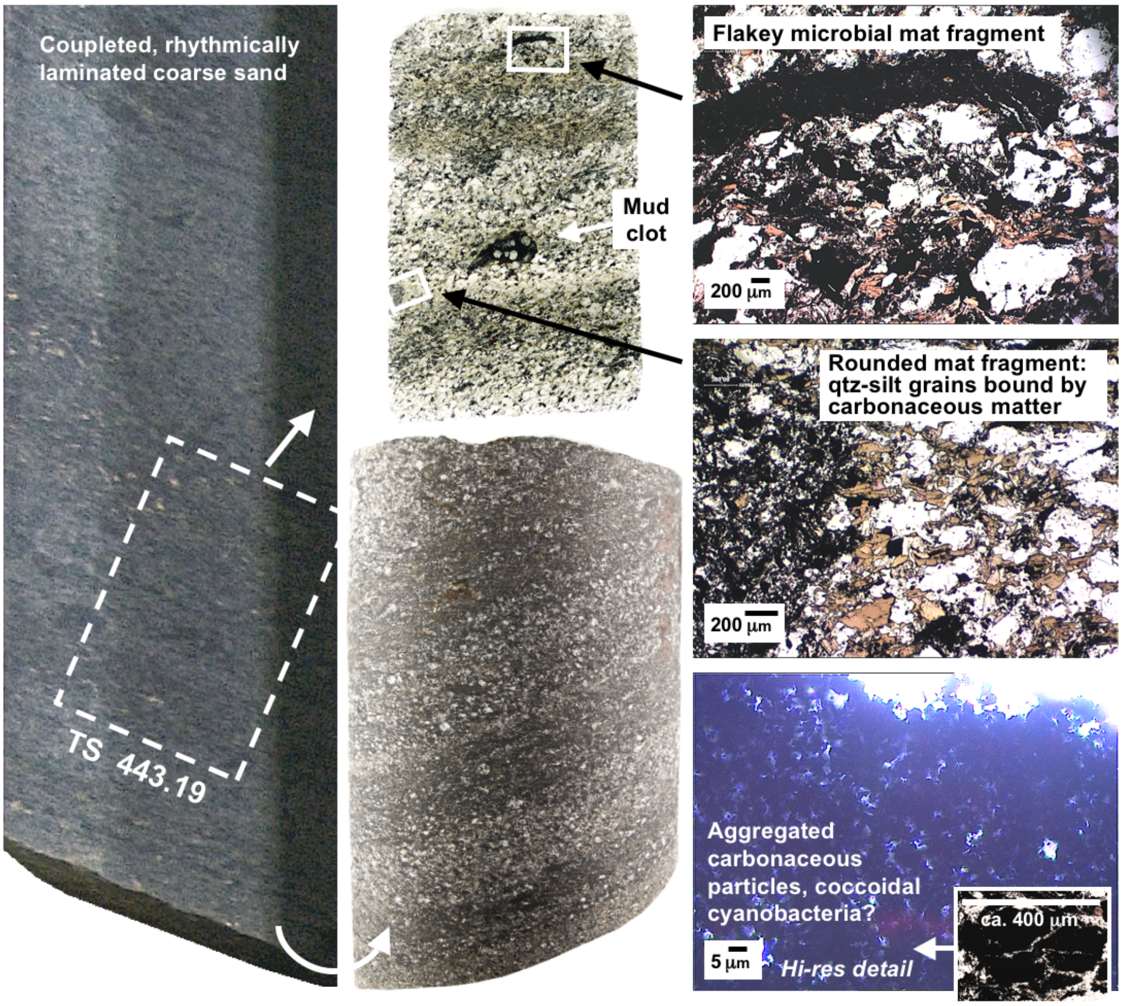

FIGURE 8. *(continued)* **B)** Close up image of thin section sample TS 443.19 representing an interluding, ”rhythmically laminated sandy package” that occur frequently in the pyrrhotitic mudstone member of TV fm (see the drill core 443.35 in Fig. 7). Rhythmic thick interlamination of coarse, micaceous ”microconglomeratic” quartz sand containing abundant carbonaceous detritus, and darker muddy clay and detrital mica-rich laminae is more distinctive in the backside of the core. Mn-rich (garnetiferous) mud clot in the optically scanned thin section image displays such cohesiveness that is interpreted to likely have originated from subaerially consolidated intertidal muds rather than eroded from the local muddy substrate. Flakey microbial mat chips and coarse quartz-silt grain binding mat fragments undisputedly originate from nearby siliciclastic intertidal flat. Rounded sand-size carbon grains composed of pure aggregates of small, nearly unimodal carbonaceous particles may represent dried remains of surficial cyanobacteria blooms.

4.5. Pyritiferous mudstone member of Talvivaara fm

The *pyritiferous mudstone member of TV fm* displays overall similar sedimentary features as the pyrrhotitic mudstone member, but gradually introduces pyrite as an increasing diagenetic and syngenetic sedimentary component (426.60–402.03 in Fig. 7.; see also Figs. 4B–D, Fig. 6B and Fig. 8C). Laminated pyrrhotite-rich lithologies in 417.92 possibly features a four-element rhythmite consisting of flood–ebb–flood–ebb -laminae (Archer 1998) representing one day, or mere semidiurnal ebb-tide couplets representing deposition during two days of the spring-tide maxima. Silt-laminated pyritiferous mudstones in 408.90–407.73 may display seasonal variations in coarser sediment influx (possibly combined with weak tidal signatures), and sandy sequence in 407.73 may represent a graded mass-flow bed, or gradually waning river-fed flood-plume sedimentation. Virtasalo et al. (2014) have obtained marine isotopic signatures from high-resolution isotopic studies of pyrite-rich laminites at 406.55–406.15 (not shown in Fig. 7).

Thinly- to microlaminated, partly biomat-like regular pyritic shales (160.43, TS 67.20) of lithologically distinctive Kuikkalampi fm (see e.g. Figs. 6C and Fig. 9) resemble much of those described by Schieber (1989), and Kuikkalampi fm may represent a coeval distal deep-water facies to Talvivaara fm, or diachronous later basinal sedimentation phase.

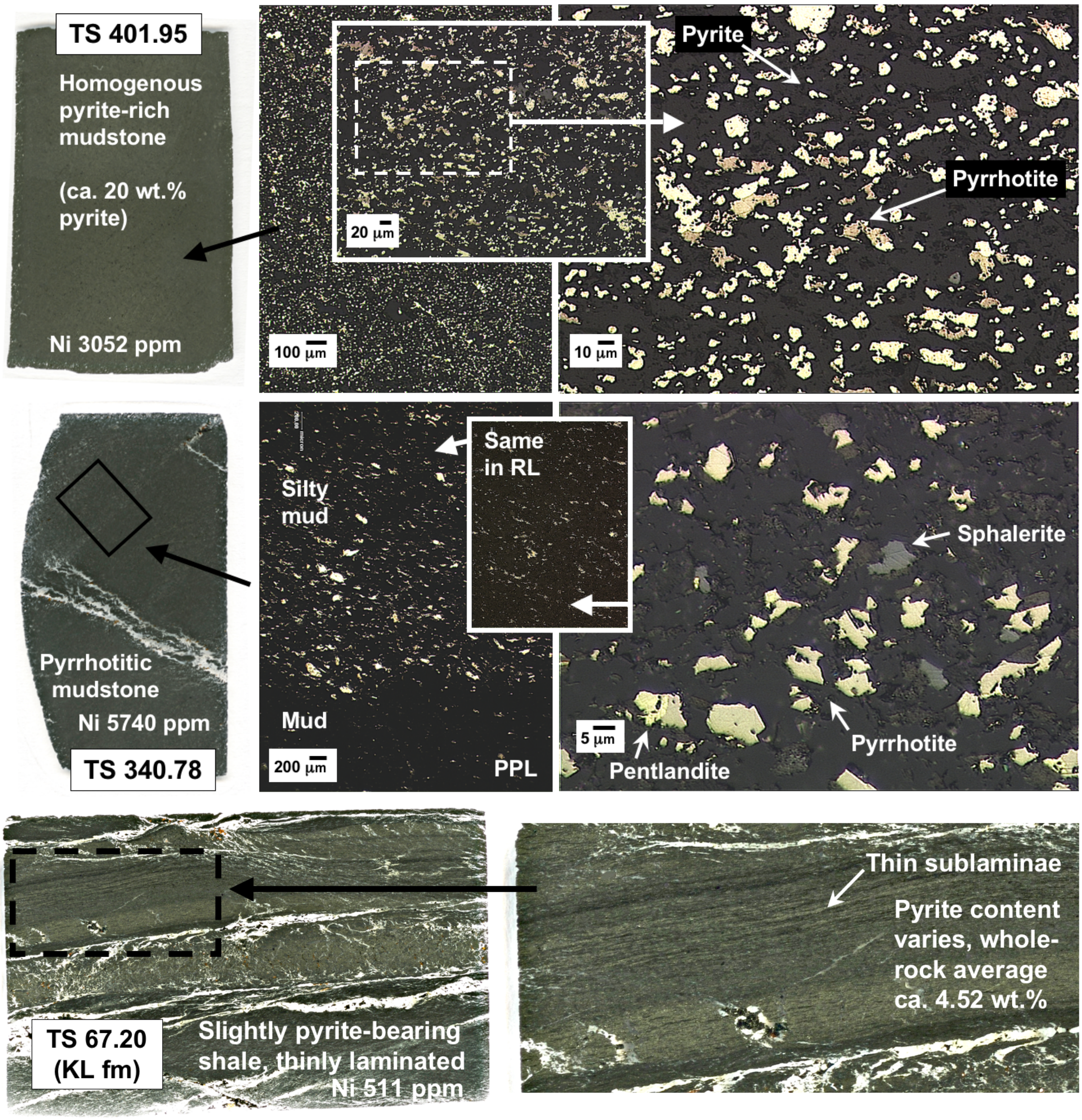

FIGURE 8. *(continued)* **C)** Thin section images exemplifying some the iron sulfidic lithofacies in drill core DDKS-010. Thin section sample TS 401.95 is from the stratigraphically continuous upper part of the pyritiferous mudstone member of Talvivaara fm. Pyrite-rich massive mudstone TS 401.95 has very high total contents of pyrite and pyrrhotite (see Fig. 6A and 402.03 in Fig. 7). Stratigraphic position of the sample TS 340.78 is unclear due to faulting, but the pyrrhotitic mudstone displaying graded silt-rich mud laminae is part of the GTK profile 3., which has the highest ”primary” Ni-Zn-Cu concentrations (see Figs. 6C and 6E–G). Plane polarized photomicrograph shows the texturally preserved contact between fine mud and a graded pulse of muddy silt rich in detrital mica; the largest flakes are metamorphically coarsened porphyroblastic phlogopite. Microphotograph in reflected light (right) shows the texture of fine-grained sulfides. Optically scanned thin section TS 67.20 represents the typical thinly laminated, pyrite-bearing non-metal enriched shales of Kuikkalampi fm. Overall, the degree of metamorphic recrystallization in Kuikkalampi fm lithologies appear to be slightly lower than in the Talvivaara formation.

5. Discussion – interpreting the provenance and sedimentary environment

Figure 9 presents TiO_2-Zr-Al_2O_3 –diagram for the GTK samples examined in the present study (Laitala *in prep.)*. A comparison with global and Fennoscandian literature data (Appendix 1) shows that the metal-enriched Talvivaara fm samples plot distinctly towards mafic–ultramafic sources. This is compatible with Lahtinen et al. (2010), who identified a significant component originating from ca. 2.1 Ga continental basalts in Finnish Lower Kaleva (Ludicovian) meta-sedimentary rocks. Fig. 9 is interpreted here as necessitating a metal-enrichment model for the Talvivaara formation that is somehow correlated with the primary composition and physical properties of sedimentary particles, not mere random external factors. Besides preservational factors, high C_{org}-levels in Talvivaara samples indicate also very prolific primary productivity, which would correspondingly require abundant nutrient supply. A cyanobacterial, bacterial, and archaeal origin for the biomass is here presumed (see e.g. Konhauser 2007). Phosphorus is one of the essential rate-limiting nutrients for photosynthetic primary producers, and riverine delivery from oxidatively weathered continental lithologies provides the largest flux of PO_4^{3-} to the oceans (Papineau 2010; Van Kranendonk et al. 2012). Basaltic rocks have high phosphorus contents, and fine clay-rich basaltic soils with adsorbed PO_4^{3-} are transported especially during flood events; estuaries may serve as short term repositories for basaltic clays, which are further preferentially remobilized, exported and hydrodynamically concentrated into nearby offshore zone (McCullogh et al. 2003; Webster et al. 2003; Douglas et al. 2005).

Laitala and Lahtinen (2014) saw in the new GTK data (Fig. 9) features that point towards Fe-Ti –rich smectitic protolith clay component derived from subaerially weathered continental basalts, which could relate to the enhanced preservation of organic carbon and metal sequestration in the Talvivaara fm sulfidic sediments (Kennedy 2002; Ossa Ossa et al. 2013). The non-metal enriched Kuikkalampi fm samples appear to be significantly lower in this Fe-Ti –rich protolith sedimentary component (Figs. 6C, 8C, and 9). Overall, integrated results of the present study indicate a near-estuarine paleoenvironmental system (see also Lahtinen 2000, p. 168), and deep-water tidal rhythmites in the Talvivaara fm attest to dynamical, complexly reprocessed proximal source for the mud–silt dominated sediments (e.g. Jaeger and Nittrouer 1995: Dalrymple and Choi 2007). Notably, iron appears to have been an unlimiting chemical reagent during the deposition of the Talvivaara formation, which likely implies both abundant detrital contribution (Krapez et al. 2003; Fralick and Pufahl 2006; Kyläkoski et al. 2013; Rasmussen et al. 2013) and ferruginous deeper water marine background conditions (Poulton and Canfield 2011; Raiswell and Canfield 2012), possibly also locally contributed by continental riverine runoff (Schieber 1987; Fralick and Pufahl 2006; Pufahl et al. 2013).

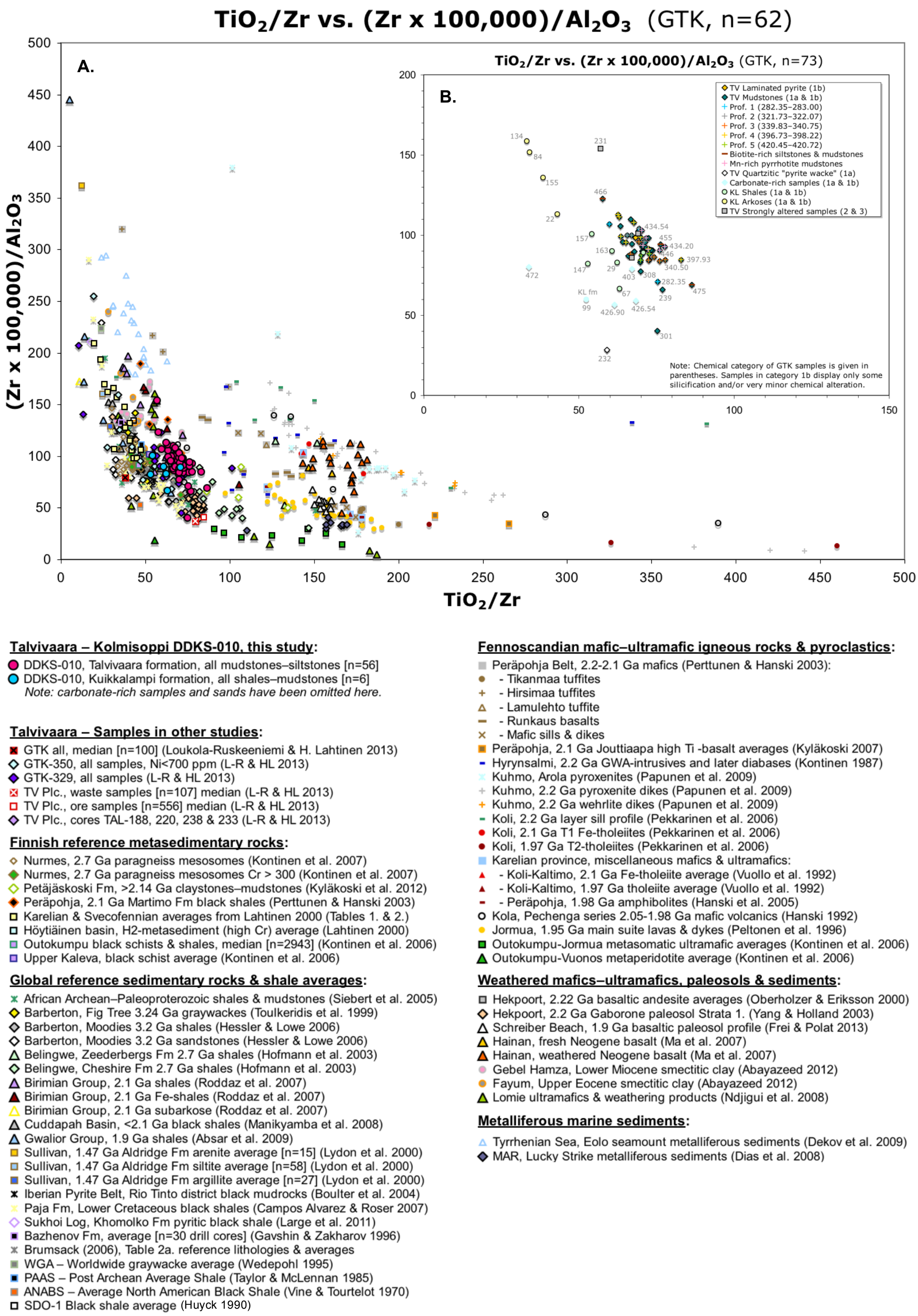

FIGURE. 9. A) TiO_2-Zr-Al_2O_3 –ratio diagram for the GTK mudstone–siltstone samples (n=62; this study) showing a distinct mafic component in the metal-enriched Talvivaara fm samples. Note that the singular KL fm sample having higher metal concentrations (sample 165.85, Ni 1905 ppm; see Fig. 6C) plots in the field of metal-enriched TV fm samples. Some Fennoscandian and global reference lithologies are plotted for comparison, the literature references are listed in Appendix 1. **B)** Insert diagram showing separately all GTK analyses (n=73; this study). The TiO_2-Zr-Al_2O_3 –diagram is adopted from Fralick (2003).

6. Conclusions

Preliminary results from this study (Laitala and Lahtinen 2014; Laitala *in prep.*) of the Paleoproterozoic Talvivaara fm (ca. 2.1–1.95 Ga) in Sotkamo, Finland, call for revising the current hydrothermal ore-genetic model for the Talvivaara Ni-Zn-Cu-Co –deposit. The new chemical data and sedimentological interpretations point coherently toward paleoenvironmental, physical exogenic surficial and redox-processes in concentrating the metals in marine, tidally dominated river influenced deep-water proximal offshore environment. Fundamentally, the enrichment and sequestration of Ni-Zn-Cu-Co-(Mo-V-U) in the C_{org} and iron sulfide-rich Talvivaara fm muds is interpreted to be linked to GOE-related major changes in the Earth's atmospheric and global surface environment, as reviewed by Holland (2005). In the present study, the metal-enriched Talvivaara fm is identified having a distinct protolith clay component derived from subaerial oxidative weathering of continental mafic–ultramafic lithologies. While the present GTK data does not trace the ultimate sources of metals or local marine sulfur, the proposed tidally resedimented paleoestuarine model for the Talvivaara fm would be consistent with elevated sulfate concentrations by nearby riverine delivery. Sulfate in the global seawater is mostly supplied by oxidative weathering of continental sulfides (e.g. Lyons et al. 2006; Farquhar et al. 2010), and it is hypothesized that the Talvivaara fm was sedimented near such delivery point. This scenario would also be consistent with the ca. 2.02 Ga emergence of sediment-hosted metal deposits in stratified, shallow basins with oxygenated sulfate-rich surface waters (Leach et al. 2010, p. 602). Indications of semidiurnal tidal rhythmicity at various stratigraphic levels of the Talvivaara formation imply unrestricted connection to the global paleo-ocean, but this would be compatible with regionally elevated metal concentrations in a narrow, likely significantly river influenced epicontinental ”Kainuu paleoseaway” situated near the Karelian craton margin.

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This work is dedicated
to the memory of my grandfather Veikko Juhani Laitala (1927–2010),
and his geologist-brother, Matti Edvard Laitala (1924–2009).

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APPENDIX 1. LITERATURE REFERENCES FOR THE TiO_2-Zr-Al_2O_3 –DIAGRAM (FIG. 9)

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