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Lithogeochemical classification of hydrothermally altered Paleoproterozoic plutonic rocks associated with gold mineralization: examples from the Nanortalik Gold Belt of South Greenland and the "Gold Line" of northern Sweden

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Introduction

There is an ongoing debate on the role of various intrusive rocks in the formation of orogenic gold and intrusion-related gold deposits (e.g. Goldfarb & Groves 2015). To classify a deposit and aid in exploration, the genetic relationship between gold mineralization and the local host rock (or a nearby intrusive rock) needs to be established. Here, we use lithogeochemistry of immobile elements to investigate the relationship between gold mineralization in Sweden and Greenland and spatially related intrusive rocks. Lithogeochemical techniques using immobile elements are widely described in the literature and have been successfully applied in mineral exploration for the classification of variably hydrothermally altered host rocks and for advanced chemostratigraphy (e.g. Barrett & McLean 1994). Although lithogeochemical rock classification is well established for the volcanic rocks series of basalt-andesite-dacite-rhyodacite-rhyolite, including those which have experienced intense alteration (Barrett & McLean 1994), suitable rock classification diagrams for altered plutonic rocks, particularly granitoids, are lacking, with the literature heavily biased towards the least altered examples. Rock classification diagrams based on major oxides (e.g. Debon & Le Fort 1982; De la Roche *et al.* 1980) are useful for unaltered rocks, however are inappropriate for altered rocks due to the mobility of major elements during alteration. For example, during alteration K, Na, Ca, Si, Fe, and Mg have been shown to be mobile due to metasomatism as demonstrated by Barrett & McLean (1994) in various case studies mainly from volcanic-hosted massive sulfide deposits (VMS). Other deposit classes such as iron oxide copper-gold (IOCG) are characterized by even stronger element mobility (e.g. Montreuil *et al.* 2013). In this contribution, we discuss how rock classification diagrams based on major elements are unsuitable for hydrothermally altered rocks and suggest more appropriate diagrams based on immobile elements. Here we present an example of classification of altered granitoid rocks and diorite that occur in the gold provinces of northern Sweden and south Greenland, spatially associated with gold mineralization ("Gold Line", Sweden; Nanortalik Gold Belt, South Greenland).

Location and geology of the "Gold Line" and the Nanortalik Gold Belt and timing of the gold introduction

The reconstruction of the Laurentia, Baltica and Amazonia continents at about 1.83 Ga (Fig. 1A-1) by Lahtinen et al. (2008) shows that the "Gold Line" is located on the Baltica continent and the Nanortalik Gold Belt is part of the Laurentia continent. Figure 1A-1 also shows the correlation of Paleoproterozoic orogens in Greenland and Fennoscandia and that the gold deposits of the "Gold Line" are part of the orogenic units of the Nordic orogeny (Fig. 1A-2, Fig. 1B) whereas the Nanortalik Gold Belt is part of the Ketilidan orogeny (Fig. 1A-2, Fig. 1C, D).

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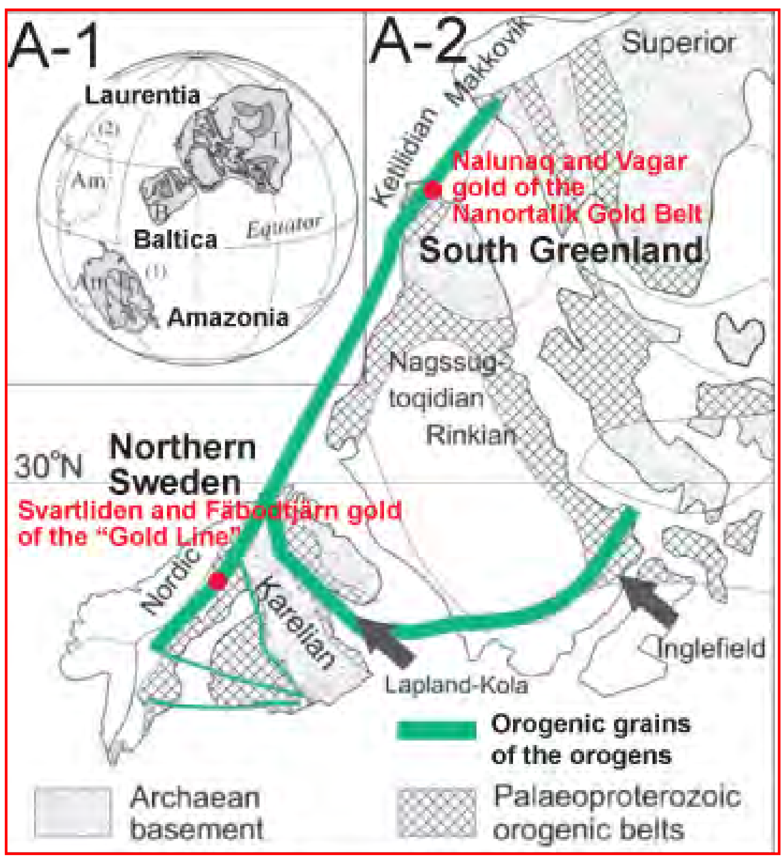

Figure 1. (A-1) Reconstruction of the position of Laurentia, Baltica and Amazonia at about 1.83 Ga. (A-2) The gold occurrences of the Nanortalik Gold Belt in South Greenland and the "Gold Line" in northern Sweden are both located on the orogenic grain of the Norden and Ketilidian orogens (modified after Lahtinen et al. 2008).

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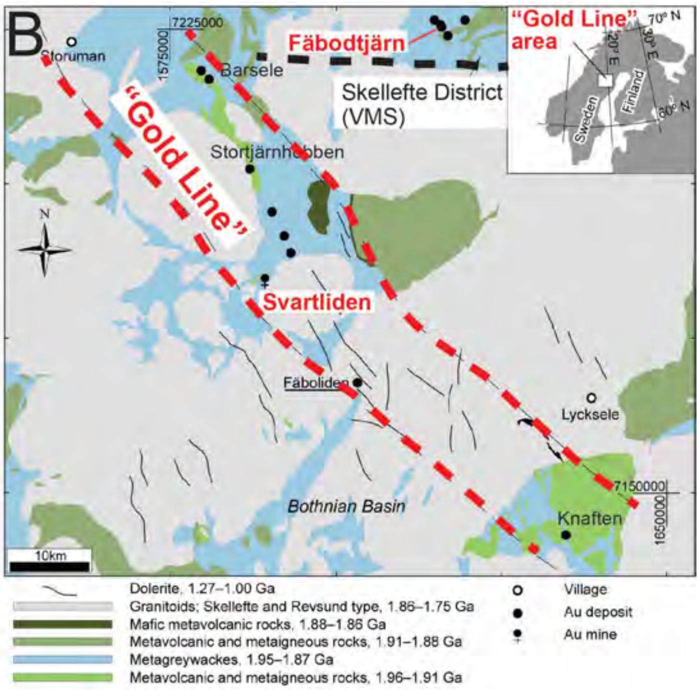
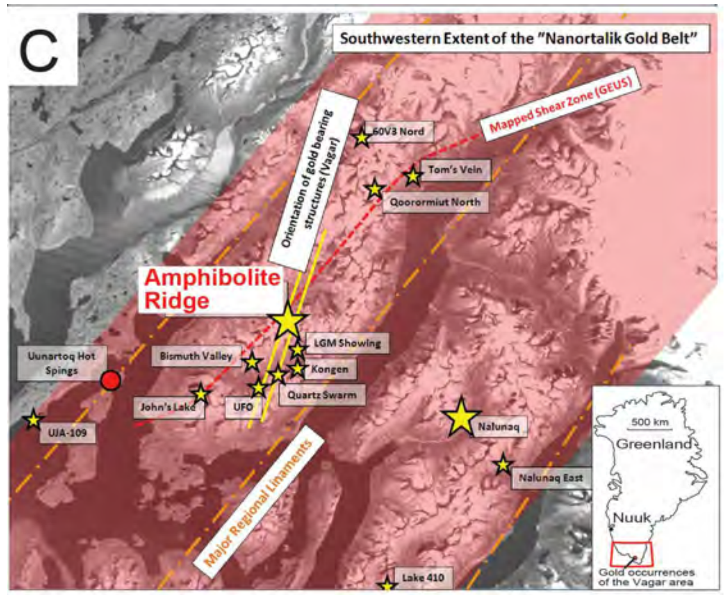
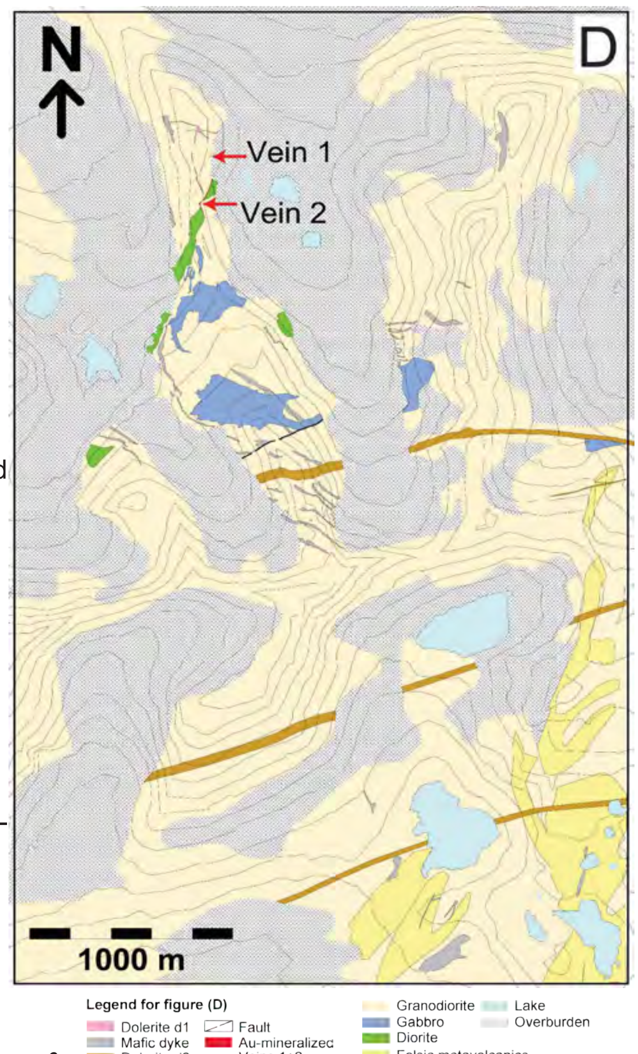
Figure 1: (B) Geological map of northern Sweden and location of the Svartliden gold mine and gold occurrences on the "Gold Line," modified after Bark (2008), Bark and Weihed (2012). (C) Location map showing in pinkish pattern the gold occurrences of the Nanortalik Gold Belt in South Greenland (yellow stars); the map also shows the main structural features (modified after Schlatter et al. 2017). (D) Geological map of the Amphibolite ridge area, the gold occurrences of Vein 1 and Vein 2 are indicated by arrows (Geodetic reference: WGS84, Projection: UTM 23N, Contour interval: 50 m. Upper left corner UTM coordinates: Northing: 6711000; Easting Easting: 497500; lower right UTM coordinates:, Northing: 6716000, Easting 500500, map from NunaMinerals A/S, 2013, in Bradley (2013).





The "Gold Line" is ca. 150 km long and 40 km wide NW-SE trending corridor, originally defined by till samples that contained elevated gold contents (Bark & Weihed 2007). The Svartliden gold deposit is located in this corridor whereas the Fäbodtjärn gold occurrence is located at the western margin of the Skellefte District located about 30 km east of the intersection of the "Gold Line" and the NW-SE trending western part of the VMS belt of the Skellefte District in the Vindelgransele area (Sundblad 2003; Allen *et al.* 1996). The geology of the "Gold Line" is dominated by granitoids and diorite of various types and ages, metavolcanic rocks and metagraywackes. Later unmineralized dolerite dykes have intruded the Paleoproterozoic rocks at about 1.26 Ga (Söderlund *et al.* 2006, Figure 1B) providing a time constraint for gold mineralization. The gold mineralization at Svartliden is hosted at the contact between metavolcanic rocks (amphibolite) and graphite-bearing metasedimentary rocks – in thin discontinuous slivers of banded iron formation and arsenopyrite-rich units with calc-silicate alteration (Fig. 2C). The gold lodes at Svartliden are related to second order regional shear structures and the mine sequence is cross-cut by a granite remobilizing the gold (Fig. 2C, Schlöglova *et al.* 2013). Other granites that occur regionally in the Svartliden area are of the Revsund and the Skellefte-Härnö type (Fig. 2B) (Andersson 2012; Billström & Weihed 1996, Schlöglova *et al.* 2013). The gold in Fäbodtjärn is located in a narrow quartz vein, hosted in a sequence of turbiditic greywackes and pelitic sedimentary rocks, spatially close to a diorite intrusion that is also gold mineralized (Öhlander & Markkula 1994; Fettweis 2015) and metamorphosed to greenschist facies (Fig. 2B).



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The Nanortalik Gold Belt in South Greenland is >150 km long and 40 km wide NE-SW trending corridor of gold occurrences and of stream sediments with elevated gold contents that range between 47 and 850 ppb (Steenfelt *et al.* 2016), corresponding to the southern margin of the Julianehåb Igneous Complex. The rocks of the Nanortalik Gold Belt are dominated by Paleoproterozoic granite and granodiorite, diorite, gabbro, metasedimentary and metavolcanic rocks and lesser dolerite, metamorphosed to amphibolite facies (Figs. 1C+D). The plutonic rocks of the Vagar host auriferous quartz veins and are spatially and possibly genetically associated with the gold mineralization (Schlatter *et al.* 2013, 2016). In the "Amphibolite Ridge" area (Figs. 1C+D, Schlatter *et al.* 2018), which is part of the Vagar exploration license, gold is located in quartz Vein 1 which is hosted in granodiorite, whereas the auriferous quartz Vein 2 is located at the lithological contact between diorite and granite (Figs. 1D and 2A). The drill hole profile (Fig. 2A) shows that gold not only occurs in the sheared quartz veins, but large portions of the host granitoid and diorite is also gold-mineralized. These intrusive bodies at Vagar are interpreted to have intruded as relatively shallow bodies based on the field observation of magmatic stoping at the locus of the pluton roof zone (Schlatter *et al.* 2013).

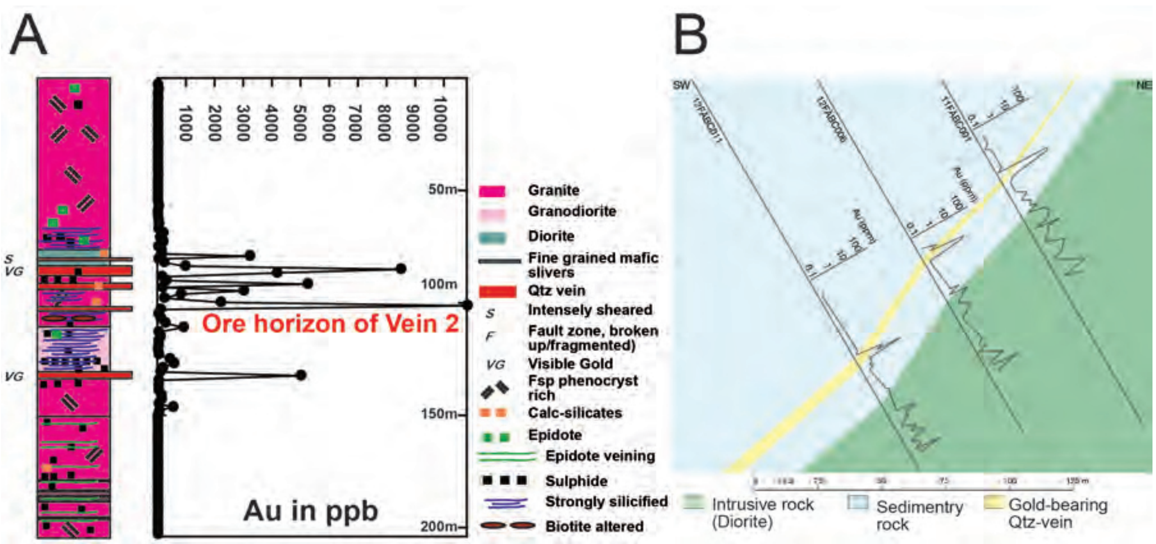

Fig. 2. (A) Tectonostratigraphic column based on drill core log across the ore horizon of the "Vein 2" target on Vagar (modified from Schlatter et al. 2013). Gold assayed by Actlabs. (B) Geological cross section of the Fäbodtjärn gold occurrence of the "Gold Line" area in northern Sweden (modified from Fettweis 2015, Fettweis & Bark 2017).

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The presence of granitoids and diorite, spatially associated with the gold is ubiquitous at Vagar, Svartliden and Fäbodtjärn. Although the gold mineralizing event of all these areas were not directly dated and such age determination remains to be carried out; at Svartliden the crosscutting and unmineralized granite yielded an age of 1.8 Ga (Persson 2011, Schlöglova *et al*. 2013). Therefore the gold mineralization at Svartliden must be older than 1.8 Ga (Figs. 2C, 3) and ore forming events of the VMS deposit of the Skellefte District (Fig. 1B) are dated at 1.9 to 1.87 Ga (Allen et al. 1996). It is conceivable that the VMS in northern Sweden were formed in a back-arc basin in an extensional setting, followed by a compressional regime in which the orogenic gold mineralization formed (Allen *et al.* 2002; see figure 2 of Allen et al. 2002)

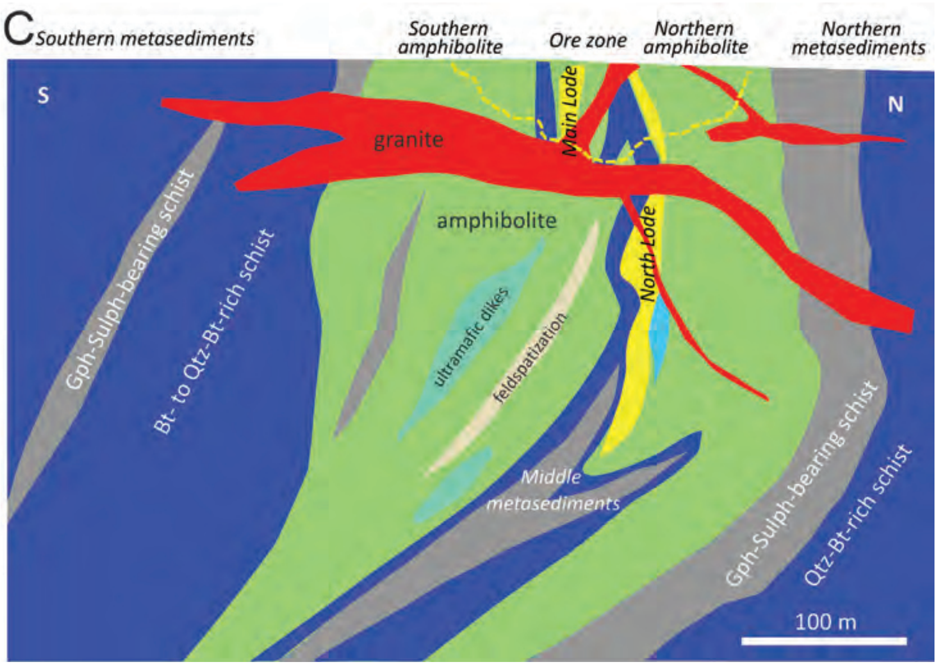

Figure 2: (C) Geological cross section of the Svartliden gold deposit of the "Gold Line" in northern Sweden (modified from Schlöglova et al. 2013).

In South Greenland, gold mineralization within the Nalunaq deposit, which produced 10.65 tonnes (375'600 oz) gold during its nine-year mine life, was directly dated at 1.783 to 1.762 Ga (Bell *et al.* 2017). The age was determined by bracketing the ages of a hydrothermal alteration preceding the gold mineralization and a pegmatite that cross cuts the gold mineralization. The granitoids and diorite that host the Vagar gold occurrences were dated at 1.85 to 1.83 Ga (Steenfelt et al. 2016). In South Greenland to date, no VMS deposits have been found, perhaps reflecting the extensive level of erosion compared to that of northern Sweden. The temporal relation between intrusive rocks and mineralizing events is provided in Figure 3; for more details, see references therein.

Sample collection, analysis and combination of data

The samples from Svartliden were collected for a M.Sc. thesis completed at the Luleå University of Technology (LTU) in Sweden (Andersson 2012) and five samples are from the collections of Dragon Mining Sweden AB (Schlöglova et al. 2013). The samples from Fäbodtjärn were collected during a M.Sc. thesis at the LTU (Fettweis 2015). The samples from the Amphibolite ridge area are from exploration carried out in the Vagar exploration license by the national and partially state-owned mineral exploration company of Greenland, NunaMinerals A/S and their consultants, Helvetica Exploration Services GmbH during field work in 2012 (Schlatter *et al*. 2013; note NunaMinerals A/S was dissolved in 2016). For this study, 47 samples from Vagar were analyzed by code "4Lithoresearch and 4BINAA" using Fusion ICP and ICP/MS for the major elements, trace elements and rare earth elements and gold on 30 g by INAA by the Activation Laboratories (Actlabs) Ltd. (Schlatter et al. 2013). Samples from Svartliden, 35 in number, were analyzed by ALS Chemex Labs Ltd. according to a multi-element characterization package + Au on a 50 g sample, using ICP-AES and LECO combustion analysis and ICP-MS (Andersson 2012; Schlöglova *et al.* 2013). From Fäbodtjärn 12 samples were analyzed by Acme Analytical Laboratories Ltd. where major oxides were quantified by lithium borate fusion with ICP-ES, while refractory and rare earth elements were reported by lithium borate fusion with ICP-MS. Precious met-

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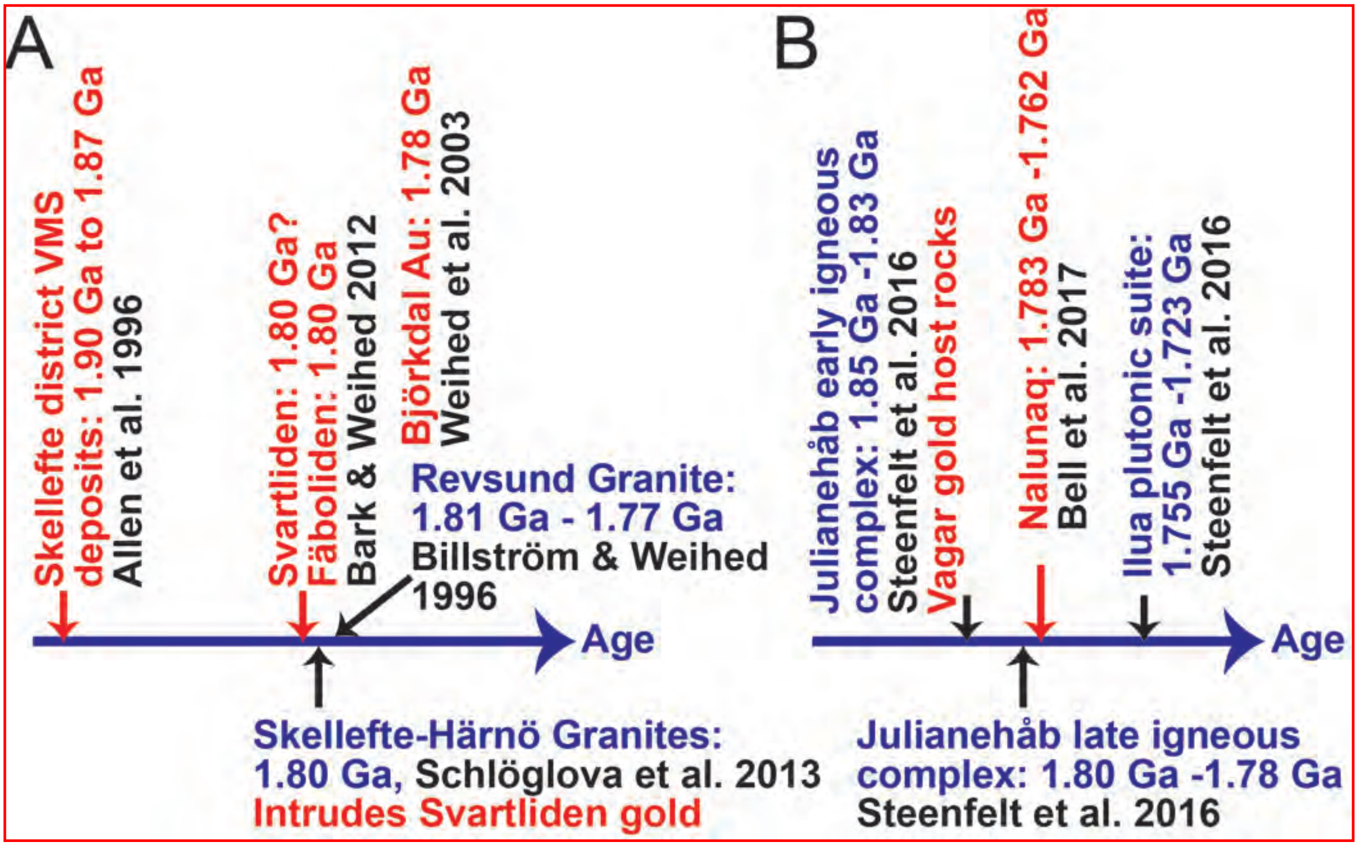

Figure 3. Timing of events of gold introduction and timing of plutonic events in (A) northern Sweden, and (B) in South Greenland (modified from Schlatter et al. 2016).

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als on 0.5 g samples and base metals were leached in hot modified aqua regia and analyzed by either ICP-ES or ICP-MS (Fettweis 2015). The data for the 94 samples from northern Sweden and South Greenland were combined (Schlatter *et al*. 2017), interpreted and plotted using the commercial software IgPet (Rock Ware, https://www.rockware.com).

Geochemical classification based on major oxides and immobile elements

The granitoid and diorite samples from all three areas (Fig. 4) were separated into samples containing less than or equal 10 ppb gold, and those greater than 10 ppb gold. Samples containing less than or equal 10 ppb gold comprise the least altered samples with gold contents similar to the crustal average and the samples that contain greater than 10 ppb gold represent hydrothermally altered samples that have interacted significantly with gold-bearing hydrothermal fluids and correspond to moderately to strongly altered rocks. This threshold of 10 ppb gold allows discrimination between least altered and altered gold mineralized samples as shown from a large geostatistical study from the Nalunag gold mine involving 233 least and 181 altered mafic rocks (Schlatter & Kolb 2011). Samples from each study area were plotted on major oxides diagrams (Figs. 4A, 4B, 4C) to demonstrate the difficulty in classifying hydrothermally altered granitoids and diorite using such diagrams. In this study and later in the text, for simplicity, we group the granite and granodiorite in the "*granitoid*" class and the quartz-diorite, quartz-monzodiorite and quartzmonzonite in the "*diorite*" class. For example, on the diagram by Debon & le Fort (1983); (Fig. 4A), it is observed that the rocks from the three study areas are not discriminating well on the diagram. Only the Fäbodtjärn samples plot mainly in the fields of quartz-monzodiorite, whereas the granitoids and diorite from Vagar plot across a range of different rock types. The geochemical classification of de la Roche (1980) that is also based on major oxides also shows large variations of rock types and the samples are not well differentiated (Fig. 4B). Finally, the diagram by Hughes (1973; Fig. 4C) that is widely used to discriminate samples into K-altered, Na-altered and least altered samples was applied to the Vagar, Svartliden and Fäbodtjärn. Samples cannot be discriminated between hydrothermally altered rock samples (filled symbols) from the least altered samples (unfilled symbols). However, on a discrimination diagram applying immobile element ratios, which was initially used to classify volcanic rocks (Pierce 1996; Fig. 4D), most samples from Vagar, Svartliden and Fäbodtjärn discriminate in tight clusters, regardless of the alteration intensity of the rock. Diorite from Fäbodtjärn plot into a distinct field, and the Vagar granitoid and diorite samples plot in two distinct fields which agrees with two different rock types (Fig. 4D). The altered granites from Svartliden are also clustered in a distinct field, which is not seen from the diagrams based on major oxides (Figs. 4A+B). Diagrams based on immobile element ratios (Fig. 4E) shows a tight clustering for the samples from the Svartliden Revsund granite and the granitoids and diorite from Vagar plot in two distinct fields, corresponding to two different granitoids and diorite occurring at Vagar. The group of Vagar samples with low Al_2O_3/TiO_2 and Zr/Al_2O_3 ratios are in the same field as the diorite samples from Fäbodtjärn (Fig. 4E) and it is conceivable that these correspond to quartz-monzodiorite, however this pattern needs be confirmed by petrography. A diagram based on the immobile elements Zr and Y is used to discriminate between tholeiitic, transitional, and calc-alkaline magmatic affinity mainly in the context of volcanic rocks (Barrett & MacLean 1994; Fig. 4F). However, this diagram is here used for discrimination of the different granitoids and diorite in this study: the Vagar rocks fall into the calc-alkaline field, the rocks from Fäbodtjärn are in the transitional field, and the three subtypes of Svartliden granitoids cluster in three distinct fields (Fig. 4F).

The geochemical assessment of the 94 granitoids and diorite has shown that these rocks are best classified in diagrams based on immobile elements (Fig. 4D, E, F). The preliminary classification diagrams based on the immobile elements Zr and Y discriminate the calc-alkaline Vagar granodiorite samples from the Svartliden and the Fäbodtjärn samples (Fig. 4F), and classification based on the immobile element ratios Al_2O_3/TiO_2 and Zr/Al_2O_3 (Fig. 4E) allow the discrimination of granitoids and diorite of different areas and two geochemically discrete granitoids and diorite at Vagar, a feature which is not apparent from major oxides diagrams (Figs. 4A and B). This lithogeochemical technique has the potential to be used in distinguishing favorable granodiorite compositions associated with gold mineralization within the study areas and thus providing a useful vector for future gold exploration.

Discussion and Conclusions and further suggested work

It is conceivable that the granodiorites predate the orogenic gold at Vagar and possibly also the diorites at Fäbodtjärn and thus "fertile" granodiorites and diorites reflect the fact they are suitable chemical or structural traps. Perhaps the composition of the Vagar granitoid and diorite, hosting significant gold mineralization (e.g. quartz veins up to 2533 ppm Au and granodiorite up to 14.4 ppm Au) and with high Al_2O_3/TiO_2 ratio (Fig. 4E), is more reactive with an auriferous fluid than other granitoids and diorite, and thus represent a more favorable

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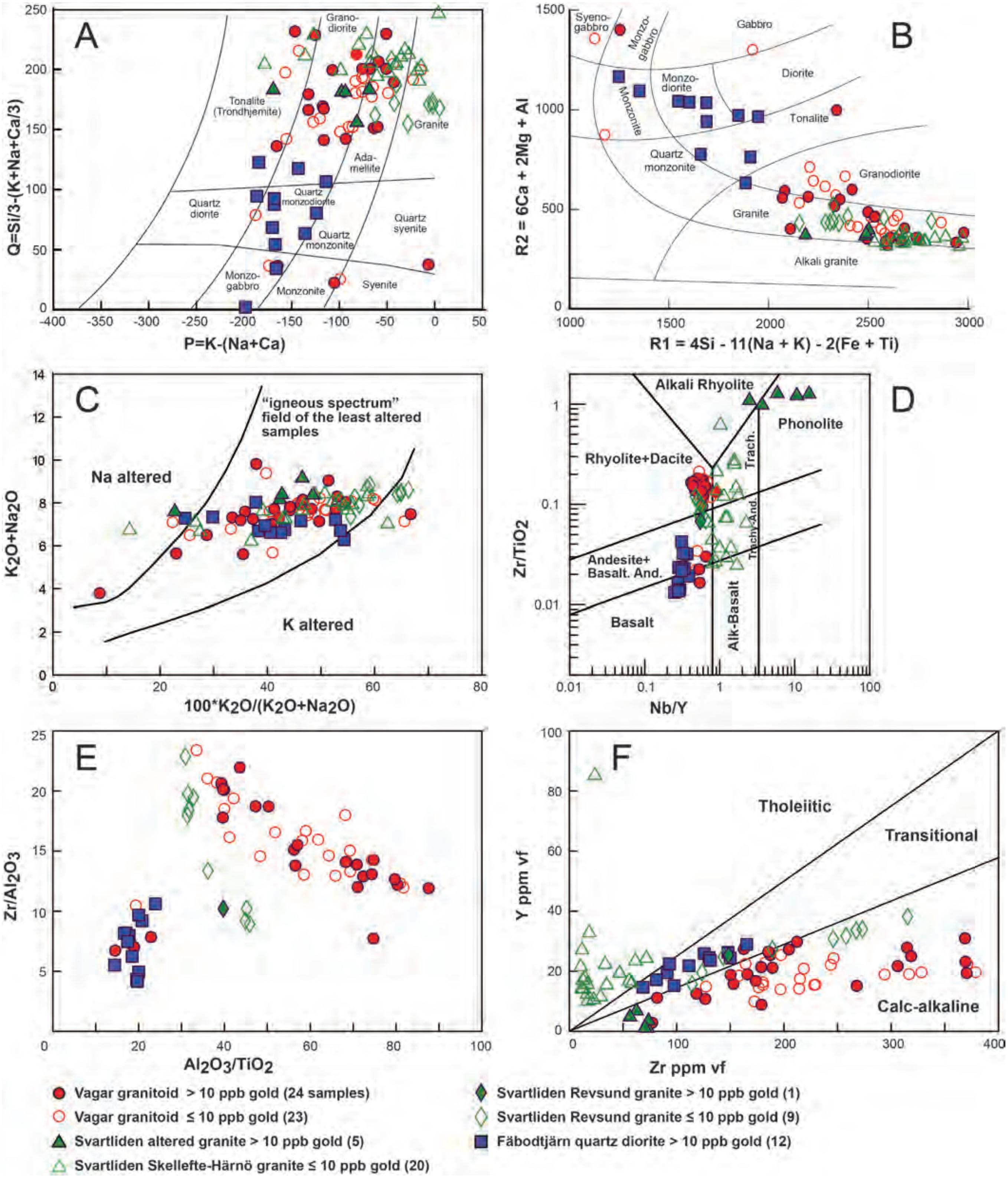

Figure 4. Lithogeochemical plots based on (A) major oxides defining rock types after Debon & Le Fort (1983). (B) Major oxides defining rock types after de la Roche et al. (1980). (C) Major oxides assessing hydrothermal alteration after Hughes (1973). (D) Immobile element ratios defining rock types after Pearce 1996. (E) Immobile element ratios plot discriminating rock types; five samples from the altered granites from Svartliden and the 20 Svartliden Skellefte-Härnö granite samples are plotting outside the diagram because the Al_2O_3/TiO_2 ratios are above 100. (F) Immobile elements assessing the affinity after Barrett & MacLean (1994). vf = volatile free basis. For (A) to (F): At Svartliden, six altered samples contain between 11 and 203 ppb gold and 29 least altered samples contain 10 ppb gold. At Fäbodtjärn twelve moderately to strongly altered samples have gold contents between 13 and 2531 ppb. At Vagar 24 moderately to strongly altered samples have gold contents between 14 and 3200 ppb and 23 least altered samples have less than 10 ppb gold. Granitoids and diorite carrying gold above 10 ppb are discriminated (filled symbols) from those that are barren (non-filled symbols).

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chemical host for gold mineralization. Another scenario is that the more competent granitoid and diorite (compared to surrounding metasedimentary rocks) simply is a rheologically more favorable site for gold deposition during deformation, providing fluid pathways during strain partitioning. Alternatively, the granitoids and diorite are genetically associated with the gold mineralization as it has been discussed elsewhere in the cases of gold deposits related to reduced granitic intrusions (Thompson & Newberry 2000).

At Svartliden, the contact of the Fe-rich metavolcanic rocks and metasediments located in a large shear zone serves as a fluid conduit and chemical trap for the mineralization. The granitic intrusion clearly postdates the mineralization and it is likely not genetically linked to the gold introduction into the system, while heat from the granite remobilizing some of the gold and enriching but also obliterating locally the ore grade (Fig. 2C). Near the Svartliden gold deposit, Fäbodtjärn diorite also occur adjacent to the gold occurrences (Fig. 1B). However, it is unclear if these intrusives are genetically related to the gold mineralizing events and/or if the intrusive bodies could have triggered hydrothermal alteration systems. Additional work that is currently carried out on the “Gold Line” includes sampling and geochemical analysis of rocks that are located outside of the hydrothermal alteration zones. New data from these fresh (least altered) rocks will be combined with the data of their altered equivalent in order to calculate mass changes caused by hydrothermal alteration (Barrett & MacLean 1994). This, in turn, will identify the elements that have the most discriminating power for distinguishing altered and the least-altered samples. More work, e.g. detailed structural geology and isotopic dating studies (U-Pb, Ar-Ar, and/or Re-Os dating) is required to conclude whether the granites are genetically related to the gold mineralization. From Svartliden some stable isotope oxygen/hydrogen data from the granites have been collected (Andersson 2012), however these data are not coupled to the gold mineralization and no conclusions can be drawn in this respect. From Vagar in South Greenland, which is an early stage exploration project, no isotopic data are available. High field strength elements-bearing phases, e.g. synchesite, allanite and monazite identified in SEM-BSE images and EDS analyses of gold bearing samples from Vagar (Schlatter et al. 2013), suggest that the hydrothermal fluid introduced REE elements together with the gold, making REE a possible pathfinder for gold exploration in the Vagar area together with the Bi and Te that is enriched at Vagar and As at Nalunaq. In the “Gold Line”, on the other hand, the gold mineralization is marked by strong enrichment in As and Sb.

Acknowledgements

The data from Fäbodtjärn presented here are from the M.Sc. thesis by Fettweis (2015) and some data from Svartliden are from the M.Sc. thesis by Andersson (2012). We would like to thank the authors for being able to use their data for new interpretations in this study. Fäbodtjärn represents also a module of the ARN Project in sub-project “Ore geology”. The ARN project “Alternative mineral raw materials in northern Sweden” is an EU project hosted at the LTU and we would like to thank ARN for organizing stimulating workshops and field excursions where, among other topics, possible geological correlations between South Greenland and northern Sweden were debated. We would like to extend our thanks to the chief-editor of **EXPLORE**, Beth McClenaghan and the reviewer, Chris Lawley, who have suggested changes that have substantially improved the paper.

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