Referee # 1 | Solid Earth Discussion

Response to referee comment (RC) on "Application of lithogeochemical and pyrite trace element data for the determination of vectors to ore in the Raja Au-Co prospect, northern Finland" by Sara Raič et al., Solid Earth Discuss., https://doi.org/10.5194/se-2021-119-RC2, 2021

General Comments

RC: The manuscript by Raic et al. on the vectors to ore in the Raja project, Finland, is an excellent study on the use of mineralogical and geochemical vectors in exploration – especially since it deals with orogenic gold systems, which have not been so extensively studied as other mineral systems. However, the paper is rather long and sometimes reiterative so I would suggest the authors to try to synthesize it.

> **Response:** Following these suggestions, the reiterative sections of the manuscript have been reduced or merged (see sections such as PCA and implications to mineralization in the discussion, as well as the conclusion section).

Specific Comments

All comments and suggestions made by the reviewer regarding typo, spelling and expression have been rephrased, accepted, and changed in the manuscript. These comprise the comments in the following lines: 11, 41, 46, 47, 49, 56, 60, 170, 785 and 851.

Comments made by the reviewer that would require a detailed response, clarification, or discussion, are addressed below.

Line 12:

As a new exploration tool for such terrains, we test the vectoring capacities of trace element and sulfur isotope characteristics of pyrite, combined with quantitative tools for whole-rock geochemical datasets.

> **RC:** Which tools?
>
> **Response:** Sentence rephrased to: […] characteristics of pyrite, combined with quantitative statistical methods of whole-rock geochemical datasets.

Lines 16–17:

The major lithologies at Rajapalot comprise variously altered and deformed calcsilicate rocks that alternate with albitized metasedimentary units, mafic volcanic rocks, mica schist and quartzite.

> **RC:** Which alteration? Albitization has affected all these rocks?
>
> **Response:** The major lithologies at Rajapalot comprise amphibolite facies metamorphosed and polydeformed calcsilicate rocks that alternate with albitic units, mafic volcanic rocks, mica schist and quartzite.

Line 40:

More than five prospects make up the broader Rajapalot Au-Co project, and this study focuses on a single prospect, Raja.

> **RC:** "More than five" looks a bit strange.
>
> **Response:** Rephrased to: Seven prospects make up the broader Rajapalot Au-Co project, and this study focuses on a single prospect, Raja.

Lines 59–60:

[…] suitable for this type of analysis, considering its capability of hosting a variety of elements of economic interest (Au, As, Ni, Co, Ag, Te, W, Sb, Mo and Se) and its compositional adaption to changes in the physicochemical parameters of a hydrothermal system (Liu et al., 2018; Large et al., 2009; Ulrich et al., 2011; Deditius et al., 2014; Keith et al., 2018; Liu et al., 2018).

> **RC:** Not all these elements are of economic interest. Delete "of a hydrothermal system".

Response: Rephrased to: […] suitable for this type of analysis, considering its capability of hosting a variety of elements of economic interest (Au, Ag, Bi, Co, Cu, Mo, Ni, Sb, Se, and Te) and its compositional adaption to changes in the physicochemical fluid parameters (Liu et al., 2018; Large et al., 2009; Ulrich et al., 2011; Deditius et al., 2014; Keith et al., 2018; Liu et al., 2018).

Line 66:
Several authors have shown that a combination of aforementioned analytical techniques also highly support refining of genetic models of ore deposits.

RC: References

Response: The following references are added in text, as well as in the reference section: Several authors have shown that a combination of aforementioned analytical techniques also highly support refining of genetic models of ore deposits (Barker et al., 2009; Hodkiewicz et al., 2009; Ulrich et al., 2011; Liu et al., 2018; Mukherjee et al., 2019; Voute et al., 2019; Meng et al., 2020; Vasilopoulos et al., 2021).

Meng, X., Li, X., Chu, F., Zhu, J., Lei, J., Li, Z., Wang, H., Chen, L., Zhu, Z.: Trace element and sulfur isotope compositions for pyrite across the mineralization zones of a sulfide chimney from the East Pacific Rise (1-2°S), Ore Geol. Rev., 116, 103209, https://doi.org/10.1016/j.oregeorev.2019.103209, 2020.

Mukherjee, I., Large, R.R., Bull, S., Gregory, D.G., Stepanov, A.S., Ávila, J., Ireland, T.R. and Corkrey, R.: Pyrite trace-element and sulfur isotope geochemistry of paleo-mesoproterozoic McArthur Basin: Proxy for oxidative weathering, Am. Mineral., 104, 1256–1272, https://doi.org/10.2138/am-2019-6873, 2019.

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

Lines 86–88:
[…] and summarized the volcano-sedimentary successions and intrusions with the following generalized lithostratigraphy (from bottom to top): (i) basaltic mafic volcanics and minor conglomerates (ii) clastic sedimentary rocks, (iii) subaerial mafic volcanics, komatiites and carbonate rocks; (iv) greywackes, carbonaceous material and sulfur-rich pelitic rocks and (v) phyllites and greywackes.

RC: Basaltic mafic is redundant. Material is not a really good geological term. Carbonaceous-bearing rocks?

Response: Rephrased to: […] and summarized the volcano-sedimentary successions and intrusions with the following generalized lithostratigraphy (from bottom to top): (i) mafic volcanics and minor conglomerates (ii) clastic sedimentary rocks, (iii) subaerial mafic volcanics, komatiites and carbonate rocks; (iv) greywackes, carbonaceous-bearing rocks and […].

Line 133:
Inferred mineral resources at Raja only, are estimated at 2.97 million tonnes @ 2.9 g/t gold with 383 ppm cobalt, which form 46 % of the gold-cobalt resources at Rajapalot (Mawson Gold Ltd., 2021).

RC: Perhaps I would say "averaging 383 ppm of Co"

Response: Rephrased to: Inferred mineral resource-estimate at Raja only are at 2.97 million tonnes @ 2.9 g/t gold and covers average 383 ppm cobalt, which form 46 % of the gold-cobalt resources at Rajapalot (Mawson Gold Ltd., 2021).

Lines 142–145:

[…] (i) Sequence 1 comprises siliciclastic, albitized and carbonatized, largely oxidized metasedimentary rocks from a continental margin setting; (ii) Sequence 2 represents a metamorphosed sedimentary sequence formed under reduced conditions consisting of pelitic turbidites, sandstones, carbonates and sulfidic carbonaceous material-bearing rocks. Mafic rocks (lava flows, dykes and volcanoclastic sediments) are common within both sequences. In the mineralized zones, domains of retrograde alteration to chlorite or epidote occur.

RC: Could you explain these oxidized sediments? I think this deserves a more detailed explanation.

Response: The oxidized part of this package most likely formed during the later stages of the Great Oxygenation Event. The oxidized state of the rocks could also have been influenced by oxidizing saline fluids, derived from the interaction with hematitic rocks that formed during the Great Oxygenation Event. Also, within the stratigraphy of the Peräpohja Belt (Kivalo Group) are inferred evaporites of the Petäjäskoski Formation (Kyläkoski et al., 2012; see reference in ms).

Lines 158–163:

The sampled drill cores are from two profiles (profile 1 and profile 2; Fig. 2b–c) from Sequence 2 of the Raja prospect. Major lithologies are mafic metavolcanic rocks (e.g. pillow basalt to amphibolite), albite-calcsilicate rocks, biotite-calcsilicate rocks, albitite, mica schist and muscovite-bearing quartzite (Fig. 2c). The zones of high-grade Au-Co mineralization are characterized by sulfide disseminations adjacent to linear, or sub-linear near-vertical structures (Cook and Hudson, 2018; Cook et al., 2020). The Raja Au-Co resource extends 240 meters parallel to strike, 950 meters down plunge reaching a vertical depth of 560 meters (Mawson Gold Ltd., 2020).

RC: I think that there is some contradiction here.

Response: The Raja Au-Co resource is formed owing to the intersection of largely vertical structures intersecting with a stratabound reactive host package resulting in a flattened prolate shape to mineralization with the long axis extending 950 meters down plunge and the in-strata intermediate axis of the ellipse up to 240 meters parallel to strike.

Line 310:

This rock commonly contains quartz and albite porphyroclasts that are rimmed by mica-rich seams and bands, which often exhibit replacement of biotite by chlorite in sheared zones.

RC: mica-rich seams and bands… don't understand

Response: The pyrite-porphyroclasts are enveloped by micas (muscovite and biotite). These sheetsilicates either form foliated seams or fine laminations. Rephrased the sentence to: This rock commonly contains quartz and albite porphyroclasts with enveloping muscovite and biotite, which often exhibit replacement of biotite by chlorite in sheared zones.

Lines 328–338:

Section 4.2.1 Alteration types

RC: This is a repetition. The term sericitic alteration is too vague. Sericite is a fine grained white mica that you don't know what is. Why not, phyllic?

Response: The metamorphic white mica is a muscovite, while the alteration white mica is more phengitic. At Rajapalot, the handing wall shows good evidence for the equivalent to the classic porphyry staged overprinting the amphibolite-facies rocks.
The section 4.2.1 was incorporated into 4.1 and section 4.2 was changed from "Alteration types" to "Ore textures and Mineralogy". The following paragraph is added to 4.1.: The most common alteration types include albitization (throughout the pre-post-syn-orogenic stages), retrograde alteration assemblages of chloritized biotite, chlorite and Fe-Mg amphiboles (syn-orogenic), sulfidation-induced formation of massive pyrrhotite and subordinate pyrite and chalcopyrite (syn-to post-orogenic), as well as sections where plagioclase is affected by the sericitic alteration characterize the latest alteration event (post-orogenic; see Table 1).

Line 418:
To achieve stable results, it is recommended to enter the principial component analysis with variables selected based on geochemical reasoning, and not with the full set of analyzed elements.

RC: By whom is recommended?
Response: reference added: […], and not with the full set of analyzed elements (see Le Maitre, 1982; Reimann et al., 2008).
LeMaitre ref. added to Reference section:
Le Maitre, R.W.: Numerical Petrology. Elsevier Scientific Publishing Company, Amsterdam, The Netherlands, 281 pp. ISBN: 978-0-444-42098-5, 1982.

Line 506:
You do not discuss at all, the mechanisms of ore precipitation despite you quote it several times along the paper.

RC: Statements on ore-formation models are included in the rephrased section 5.4 Signatures of sulfur isotopes in pyrite and ore-forming processes.

Line 623:
Pyrite A, which has the highest Co/Ni ratios, displays the heaviest $\delta^{34}S$ signatures $\delta^{34}S$ (1.3 ‰ to +5.9 ‰), contrasting with pyrite B (-1.8 ‰ to +7.3 ‰) and pyrite C (-1.2 ‰ to +7.4 ‰; Fig. 13b; Table 3).

RC: Perhaps highest instead heaviest…
Response: Rephrased: Pyrite A, which has the highest Co/Ni ratios, displays positive only $\delta^{34}S$ signatures (+1.3 ‰ to +5.9 ‰), contrasting with pyrite B (-1.8 ‰ to +7.3 ‰) and pyrite C (-1.2 ‰ to +7.4 ‰; Fig. 13b; Table 3).

Line 643.
Regional pre-orogenic albitization, caused by diagenetic and basinal brines, prepared the country rocks for a possible pre-enrichment of metals and for later Au-mineralizing processes.

RC: I am a bit surprised that you state that albitization is caused by sedimentary brines during diagenesis. I guess that many people would disagree with this. Could you expand this discussion a bit, perhaps in other place of the paper? Or at least add some references.
Response: In Eilu et al., (2003): Several deposits in the CLGB, the Kuusamo belt and the Peräpohja belt are associated with albitization along major structural features (Pankka and Vanhanen, 1992). In these greenstone belts the early spilitization and diagenetic albitization are then overprinted by a more extensive albite alteration, which is interpreted to be the result of a of greenstone belt-scale hydrothermal circulation of magmatic and/or basinal brines prior to or during the peak deformation (Pankka and Vanhanen, 1992; Vanhanen, 2001).

At Rajapalot we can see the preservation of fine laminar structure in some rocks that are not fabric destructive. The driving force for country rock pre-preparation are basinal saline-fluids, along with the probably localized heating around large mafic lavas and sills. *Line 643 is rephrased to:* Regional pre-orogenic or early-metamorphic albitization, which predates the peak deformation and gold mineralization, was caused by greenstone belt-scale hydrothermal circulation of magmatic and/or basinal brines (see Eilu et al., 2003), which prepared parts of the country rocks for a possible pre-enrichment of metals and for later Au-mineralizing processes (Pankka and Vanhanen, 1992; Vanhanen, 2001).
Reference added to refences section:

Pankka, H.S. and Vanhanen, E.J.: Early Proterozoic Au-Co-U mineralization in the Kuusamo district, northeastern Finland, Precambrian Res., 58, 387–400, https://doi.org/10.1016/0301-9268(92)90126-9, 1992.

Lines 659–661:

These rocks underwent several stages of alteration, such as albitization, chloritization and sericitization and have different rheological properties (brittle and ductile), indicating that rheology has an impact on the metallurgical processes (Farajawicz & Cook, 2021).

RC: Rheology and metallurgical processes… can you explain this a bit more?

Response: Rephrased to: These rocks underwent several stages of alteration, such as albitization, chloritization and sericitization producing widely varying rheological hosts to mineralization (Farajawicz & Cook, 2021). These contrasting host rheologies will play a significant part in the design of suitable crushing circuits capable of releasing gold and cobalt into chemical or flotation treatment cells

Lines 740–745:

The most abundant trace elements in pyrite are Co (up to 3.6 %), Cu (up to 1.1 %), As (up to 0.77%), Ni (up to 0.38 %), Se (up to 0.15 %), Mo (up to 713 ppm), Ag (up to 659 ppm), W (up to 242 ppm), Tl (up to 123 ppm), Te (up to 110 ppm), Bi (up to 94 ppm) and Au (up to 4.38 ppm). Considering that divalent cations, such as Cu^{2+} (0.54 Å), Co^{2+} (0.65 Å) and Ni^{2+} (0.69 Å) are involved in isovalent substitution with Fe^{2+} (0.61 Å), their anomalous concentrations within the pyrite structure are less surprising (George et al., 2018). Cations involved in coupled heterovalent substitution of $2Fe^{2+}$ are Cu^{+}, As^{3+}, Mo^{4+}, Ag^{+}, $W^{6+}$and Au^{+}, Au^{3+}, Tl^{+}, Bi^{3+} (Chouinard et al., 2005 in George et al., 2018; Deditius et al., 2009). Elements involved in the anion substitution of S are As, Sb, Se and Te, as they can play the role of cations and anions (George et al., 2018).

RC: this repeats what was said above. Try to clear it.

Response: Following the suggestions of the reviewer this section was shortened to avoid repetition.

Line 767:

While the latter PCs are capable to describe substitution processes within the pyrite structure, which is a valuable asset for geometallurgical purposes, the PC3 points out that some grains could show an association between Au and As, when considering their negative loadings (see Fig. 12b).

RC: Again, I don't understand why geometallurgy is quoted here.

Response: The phrase "which is a valuable asset for geometallurgical purposes" is removed from the sentence., and rephrased to: "The PC3, however, points out that some grains could show an association between Au and As, when considering their negative loadings (see Fig. 12b)".

Line 780:

According to Dmitrijeva et al. (2020), the significant W and Mo signals in pyrite represent newly precipitated sub-micron-scale scheelite and molybdenite phases that are the products of a coupled dissolution-reprecipitation reaction of a parent W-Mo-bearing hematite

> **RC:** I think that here there is a misunderstanding of the paper by Dmitrijeva et al. (2020) paper. I don't understand what is the link here with hematite – not present in Raja to my knowledge.
>
> **Response:** When considering the bituminous and graphitic rocks at Rajapalot, the molybdenum is clearly tied to organic material (e.g. flakes of Mo in peculiar bitumen shapes; chemistries also point to a reduced black shale precipitation of Mo). Regarding the W, it is possible that the scheelite and wolframite are sourced from the granitoids (along with boron). Another W-source could be from W-evaporites as discovered in Searles Lake (California). This issue is currently being studied and investigated by another working group at the GTK and will hopefully soon provide more clarity.

Line 789–791:

In order to determine whether the relatively high concentration of all analyzed trace elements in Raja pyrites are due to nanoparticles would require detailed high-resolution transmission electron microscopic measurements, which however is beyond the scope of this study.

> **RC:** This is not true – with LA ICPMS you can usually detect nanoinclusions unless evenly disseminated.
>
> **Response:** The reviewer is correct, nanoparticles are not likely going to be seen in the laser profile, since we are cutting down about 1 micron per second. Bigger inclusions will be seen, however, if they are a few nanometers, it is difficult to determine whether they are dispersed uniformly.

Line 802:

The negative shift in sulfur isotopic values and the large within-pyrite variations of $\delta^{34}S_{VCDT}$values may indicate variation in relatively oxidizing and reducing conditions in the fluid system, related to local magmatic-hydrothermal and sedimentary sources, respectively (Hodkiewicz et al. 2009; Molnár et al, 2016b).

> **RC:** This is highly unlikely – for having such variations in the SO4-H2S ratios you need to be in the stability field of sulfates… check some relevant references. Perhaps reflects mixing between magmatic and sedimentary sources. The positive values perhaps due to the inheritance of sulfur from a system with biogenic reduction of sulphate in a partially closed system.
>
> **Response:** Sentence is rephrased to: The significant changes in Co/Ni ratios in pyrite B, and the wider range in sulfur isotopic values (-1.8 ‰ to +7.3 ‰), as well as the erratic within-grain variations of $\delta^{34}S_{VCDT}$ (up to 4‰.), may be caused by the variation in the redox conditions in the fluid system (Ohmoto, 1972; Hodkiewicz et al. 2009; Molnár et al, 2016b). Such a variation is not uncommon in magmatic hydrothermal systems with predominantly magmatic origin of sulfur. However, mixing of sulfur from different sources (e.g., from magmatic fluids and from metasediment-related fluids) cannot be excluded and in this latter case the elevated $\delta^{34}S_{VCDT}$ values may indicate influx of sedimentary sulfur produced by sulphate-reducing bacteria.
>
> Ohmoto (1972) reference added to reference section:
>
> Ohmoto, H.: Systematics of Sulfur and Carbon Isotopes in Hydrothermal Ore Deposits, Econ. Geol., 67, 551–578, 1972.

Line 809:
The documented negative $\delta^{34}S_{VCDT}$ values for pyrite C (-1.2 ‰ to +7.4 ‰), as well as the elevated concentrations of redox sensitive elements (Ni, Cu, W Ag Hg, Mo and Zn) may also indicate the occasional shift of conditions to a more oxidizing state.

> **RC:** The d34S depletion is very low and within the range of magmatic rocks, either leached from or degassing.
>
> **Response:** The reviewer is correct with the statement that the d34S variation is small and still within the magmatic source range. The statement in line 809 is related to the variation in redox-sensitive element concentrations that is used to strengthen the argument that S-isotope variation reflects minor changes in redox conditions.

Line 816-onwards:
Section 5.5 Implications for mineral exploration

> **RC:** This is dominantly a repetition of what has said before and a lot of vague statements. I would delete most of it and merge the key info with the conclusions
>
> **Response:** Following this suggestion, the sections 5.5 and 6 are merged and shortened to section 6. Conclusions and implications to mineral exploration.