Reply on RC2

Sara Raič et al.

Author comment 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-AC2, 2021

Referee # 2 | 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: This manuscript, focussing on the Raja prospect, Finland, is an excellent study demonstrating the use of geochemical techniques and vector determination to aid in targeted mineral exploration. There is an abundance of detail throughout, though as a result the manuscript is longer than necessary. The authors should reduce the length of the text and avoid unnecessary background information. They should also avoid repetition, particularly in relation to principal component analysis discussions.

Response: Taking the reviewers comment regarding the length, repetition and too detailed background information into account, section of the manuscript to which this comment applies to have been reduced, such as the PCA and implications to mineralization parts of the discussion, as well as the conclusion.

RC: Within all figure captions, the analytical data sources should be stated – eg. In Figure 11, it should be stated that the data come from LA-ICP-MS analysis of pyrites. This allows the reader to assess the figures without reference to the text (they should be able to stand alone). Do this for all figure captions, where appropriate.

Response: The analytical data sources have been stated within figure captions that it applies to (Figs. 11 and 12), as suggested by the reviewer.

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: 20, 25, 28, 81, 144, 416, 422, 432, 509, 519, 552,576, 620, 814, 851, 857, 872 and 883.

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

Line 40:

An example of this kind of gold mineralization has recently been discovered in the Paleoproterozoic Peräpohja belt, within the Rajapalot project area owned by the Mawson Gold Ltd (centered at coordinates 3,408,707E by 7,372,441N of the Finnish coordinate system KKJ3).

RC: Given the international scope of the journal, please express coordinates using a globally utilized coordinate system.

Response: Changed to: […] (centered at coordinates 408750.412294E by 7369184.18986N of the EUREF_FIN_TM35FIN coordinate system).

Lines 82–84:

The depositional history of these Karelian basins coincides with the Great Oxygenation Event, which created favorable conditions for a pre-concentration of metals (e.g. Co, Cu, Ni, Mo and Au) in sulfidic sediments, as well as the deposition of carbonaceous material (Melezhik et al. 2013).

RC: Numerous peer reviewed publications support the statement regarding the favorable conditions for the concentration of metals in basinal deposits during periods of atmospheric oxygenation, including Lyons et al., 2014; Large et al., 2014, 2015, 2017; Gregory et al., 2017; Johnson et al., 2017; Armstrong et al., 2018. Reference to some of these works should be made.

Response: Suggested references were included in the text, as well as in the reference section:

Armstrong, J.G.T., Parnell, J., Bullock, L.A., Perez, M., Boyce, A.J., Feldmann, J.: Tellurium, selenium and cobalt enrichment in Neoproterozoic black shales, Gwna Group, UK: Deep marine trace element enrichment during the Second Great Oxygenation Event, Terra Nova, 30, 244–253, https://doi.org/10.1111/ter.12331, 2018.

Gregory, D.D., Lyons, T.W., Large, R.R., Jiang, G., Stepanov, A.S., Diamond, C.W., Figueroa, M.C., and Olin, P.: Whole rock and discrete pyrite geochemistry as complementary tracers of ancient ocean chemistry: An example from the Neoproterozoic Doushantuo Formation, China, Geochim. Cosmochim. Ac., 216, 201–220, https://doi.org/10.1016/j.gca.2017.05.042, 2017.

Johnson, S.C., Large, R.R., Coveney, R.M., Kelley, K.D., Slack, J.F., Steadman, J.A., Gregory, D.D., Sack, P.J., Meffre, S.: Secular distribution of highly metalliferous black shales correspond with peaks in past atmosphere oxygenation, Miner. Deposita, 52, 791–798, https://doi.org/10.1007/s00126-017-0735-7, 2017.

Large, R.R., Halpin, J.A, Danyushevsky, L. V., Maslennikov, V.V., Bull, S.W., Long, J.A., Gregory, D.G., Lounejeva, E., Lyons, T.W., Sack, P.J., McGoldrick, P.J., Calver, C.R.: Trace element content of sedimentary pyrite as a new proxy for deep-time ocean-atmosphere evolution, Earth Planet. Sc. Lett., 389, 209–220, https://doi.org/10.1016/j.epsl.2013.12.020, 2014.

Large, R.R., Gregory, D.D., Steadman, J.A., Tomkins, A.G., Lounejeva, A., Danyushevsky, L. V., Halpin, J.A., Maslennikov, V., Sack, P.J., Mukherjee, I., Berry, R., Hickman, A.: Gold in the oceans through time, Earth Planet. Sc. Lett., 428, 139–150, https://doi.org/10.1016/j.epsl.2015.07.026, 2015.

Large, R.R., Mukherjee, I., Gregory, D.D., Steadman, J.A., Maslennikov, V. v., Meffre, S.: Ocean and Atmosphere Geochemical Proxies Derived from Trace Elements in Marine Pyrite: Implications for Ore Genesis in Sedimentary Basins, Econ. Geol., 112, 423–450, https://dx.doi.org/10.2113/econgeo.112.2.423, 2017.

Lyons, T.W., Reinhard, C.T., Planavsky, N.J.: The rise of oxygen in Earth's early ocean and atmosphere, Nature, 506, 307–315, https://doi.org/10.1038/nature13068, 2014.

Lines 99–101:

RC on Figure 1: Excellent figure and very detailed, though this should be a full page landscape

figure to ensure detail is not illegible in final publication.

Response: Following the suggestion of the reviewer, Figure 1 is rearranged, in order to be completely clear and legible for the reader.

RC on Figure 1 caption: Data sources for maps (a) and (b) require citations.

Response: Sources added: (a) Geologic map of the main bedrock units of the eastern part of the Fennoscandian Shield and the Peräpohja belt as highlighted area (black rectangle). Simplified geological map is based on Koistinen et al. (2001) (b) Geologic map of northern Finland showing Archean and Proterozoic rocks. The Rajapalot Au-Co project is located within the shaded rectangle. Simplified map is modified from the Bedrock of Finland – DigiKP (2021; digital map database of the Geological Survey of Finland).

Both references are added to reference section:

Koistinen, T., Stephens, M. B., Bogatchev, V., Nordgulen, Ø., Wennerström, M. & Korhonen, J. (comp.): Geological map of the Fennoscandian Shield, scale 1:2 000 000. Trondheim: Geological Survey of Norway, Uppsala: Geological Survey of Sweden, Moscow: Ministry of Natural Resources of Russia, Espoo: Geological Survey of Finland. https://gtkdata.gtk.fi/kalliopera/index.html#, 2001.

Bedrock of Finland – DigiKP: Digital Map Database, Geological Survey of Finland (GTK): https://gtkdata.gtk.fi/kalliopera/index.html#, last access: 06.12.2021.

Lines 205–222:

Trace element analyses in pyrite were performed by a laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS) at the Geological Survey of Finland (GTK), using a Nu AttoM single collector (SC)-ICPMS (Nu Instruments Ltd., Wrexham, UK) and an Analyte Excite 193 ArF laser-ablation system (Photon Machines, San Diego, USA). The laser was run at a pulse frequency of 10 Hz and a pulse energy of 5 mJ at 30% attenuation to produce an energy flux of 2.5 J/cm2 on the sample surface with a 50 μm spot size. Each analysis was […].

RC: Was a hydrogen reaction cell utilized in the LA-ICP-MS analysis, to remove selenium analysis interferences? If not, the potential influence of this interference needs to be accounted for in the discussion. If a reaction cell was utilized in the analyses then this should be stated.

Response: We are aware of the formation of Ar-based polyatomic ions that affect the determination of 77,78,80Se+ ($^{40}Ar^{36}Ar^{1}H+$, $^{40}Ar^{38}Ar+$, and $^{40}Ar^{40}Ar+$). However, all of these interferences are gas blank related, i.e., they are generated in the ICP and do not result from the laser ablation process. Consequently, since all of our analyses were acquired using TRA (Time Resolved Analysis) that in every case starts with a gas blank measurement, all gas-related polyatomic interferences are removed prior to concentration calculation. No reaction cell is required.

Lines 229–235:

One pyrite standard was used for external standard bracketing (PPP-1; Gilbert et al, JAAS, 2014) and the in-house standards Py1 and Py2 were used for quality control, both previously measured by gas mass spectrometry. For Py1, with a $\delta^{34}S_{CDT}$(‰) reference value of -0.6 ± 0.3 ‰ (1s) we measured an average value of -0.6 ± 0.5 ‰ (1s, n=26). For Py 2 with a$\delta^{34}S_{CDT}$(‰) reference value of -0.3 ± 0.3 ‰ (1s), we measured an average […].

RC: Insert the reference value and analysed value for the PPP-1 external standard. The internal standards utilised in the S-isotope analysis calibration/QC span a very narrow δ34S range (-1.2 to 0 ‰, including errors). The δ34S values found during the sample

analyses range outside the range of the standards (-1.76 to 7.40 ‰), making the calibration at the farthest ranges less reliable. This is a minor point as the difference between the standards and sample values is not substantial, but it is not good practice.

Response: The external standard has a certified value of d34SV-CDT= +5.3 ± 0.2‰ and the quality control standard are -0.6 ± 0.5‰ and -0.3 ± 0.3‰, so the isotopic range (about 6‰) is very close to the range of the samples (-1.76 to 7.40 ‰). We also routinely analyze an additional in-house quality control standard of pyrrhotite composition, having a value of +5.6‰, with similar accuracy to the two in house pyrites standards analyzed in this study.

Line 272:

In practice it turned out to work well, when only considering eigenvectors with eigenvalues > 1.

RC: "In practice it turned out to work well" – this is an opinion with no clear justification or scientific merit to the statement. Please rephrase.

Response: Sentence is deleted, but the statement eigenvalue >1 is included in the previous sentence (and Jolliffe, 2002 reference is added): After this standardization, the data matrix is used for the computation of the correlation matrix PCA. In order to assure that most of the data variability is preserved, only principal components with large **eigenvalues ()** are considered (see Kaiser, 1960; **Jolliffe, 2002**).

Jolliffe, I.T.: Principal Component Analysis, Second Edition, in: Springer Series in Statistics, edited by: Bickel, P., Diggle, S., Fienberg, Krickerberg, K., Olkin, I., Wermuth, N., Zeger, S., Springer, New York, USA, pp. 487, ISBN 0-387-95442-2, 2002.

Lines 277–279:

Out of the 50 elements analyzed within the whole-rock geochemical dataset, a subset of 12 elements was used (As, Au, Co, Cu, Mo, Ni, Se, Sn, Te, Tl, U and W). From the 61 elements analyzed in pyrites, a total of 12 were used to produce geochemical groupings with the PCA (Ag, As, Au, Bi, Co, Cu, Mo, Ni, Se, Te, Tl and W).

RC: Why were the subsets of 12 elements used different in the whole rock vs the LA-ICP-MS data? Did the statistical method not work on certain elements, or were these analyses not available from the given analytical methods?

Response: For the two different datasets, only elements were used that would contribute to the building of a predictive model when using the algorithms of the PCA. For this purpose, one has to consider a dimensionality reduction of our data matrix. To achieve dimensionality reduction, elimination of a subset of variables must be considered, rather than the elimination of entire observations. For this purpose, the following must be considered: missing data (gaps in data collection, high proportion of missing values, other

errors), low or zero variance throughout (normalized) observations, or high correlations between variables (too many similar features are not useful in enhancing the predictive power of the model). When considering all these features ("pre-modelling" à covariance matrix, correlation matrix, missing values, etc.), the two different subsets of variables that were used in this study, could be identified as the "key" elements for the PCA.

Lines 327-335:

Section **4.2.1 Alteration types**

RC: This section does not appear to be providing results of the new analyses, but summarising the alteration events as identified in previous works. If there are no new results, this should be in the intro and/or discussion sections. If evidence of this alteration has been observed, then this information should be incorporated into sections 4.1 or 4.2.2. Either way, this section should be incorporated elsewhere within the text or removed.

Response: Following the suggestion of the reviewer, 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 section is added to 4.1.: The most common alteration types include albitization (pre-post-syn-orogenic), 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 358:

Pentlandite occurs as flame-like exsolution lamellae (few microns) or as anhedral inclusions in pyrrhotite.

> **RC:** Provide a numerical value for the pentlandite exsolution lamellae.

Response: The size of exsolution lamellae is <20µm; changed to: Pentlandite occurs as flame-like exsolution lamellae (<20µm) or as anhedral inclusions in pyrrhotite.

Line 360:

The Bi-Te-rich phases also occur along grain contacts with biotite (Fig. 5d). Given the small grain size of the Bi-Te-rich phases, no useful analyses could be produced to define their respective mineral names.

RC: Do the numerous Bi-Te-rich phases have a consistent composition (and thus potentially mineralogy?), or are they highly variable? As is mentioned, the size precludes accurate mineral identification, but does the composition appear similar across most/all of the Bi-Te-rich phases?

Response: Unfortunately, no useful analyses could be produced for the Bi-Te-rich phases given their small grain size. However, identification with the SEM gave a composition between 18.61 and 34.38 wt.% for Bi, and a Te-composition between 13.10 and 54.73 wt.%. Additional components that showed a signal are Co, Fe, Mo, As and S (when in assemblage with cobaltite, sulfides, and molybdenite). These estimates made by the SEM indeed show a compositional variation. It is however difficult to determine whether the varying chemistries reflect separate mineral phases or are the result of inaccurate signals due to grain size.

Figure 5: Above Line 365

RC on Figure 5: Are all 12 images necessary to convey the extent of mineralisation? This seems excessive.

Response: As suggested by the reviewer, the number of photomicrographs in Figure 5 was reduced from 12 to 6. The figure caption is adjusted accordingly-

Line 514:

Geochemical gradients recognized from the correlation of alteration mineralogy with Au- and Co-grades in MER dimensions exhibit distinct trends […].

RC: "MER" – this acronym has not been stated in the text. This should be given in brackets after the term on line 508.

Response: The acronym "MER" is first mentioned in section 3.3.2 Molar element ratio analysis, **Lines 283–285:** Molar element ratio (MER) analysis and corresponding plots of $3K/(Al + Mg + (Fe - S)$ *versus* $Al/(Al + Mg + (Fe - S)$, and $(Na + K)/Al$ *versus* Na/Al, are the variables and ratios that best describe the observed alteration assemblages.

Figure 10: Above Line 525

RC on Figure 10: Figure 10 – (e) and (f) require legends for Au and Co. Presumably they are the same as those used in (b) and (c), but this is not clearly stated nor very obvious.

Response: Following the suggestion of the reviewer, it is clarified in the Figure caption that the legends from Figs 10 b-c are applicable for Figs. 10 e-f. Figure caption is rephrased to: Figure 10: Graphical presentation of mass transfer processes at Raja in molar element ratio diagrams in correlation with Au-and Co-grades. Axes are molar ratios. Diagrams are taken from Stanley (2017). Molar ratio plots of $3K/(Al+Mg+(Fe-S)$ *versus* $Al/(Al+Mg+Fe-S)$ classified according to (a) lithologies, (b) Au-concentrations (in ppm) and (c) Co-concentrations (in ppm). General element ratio diagrams using $(Na+K)/Al$ *versus* Na/Al and classified according to (d) lithologies, (e) Au-concentrations (in ppm) and (f) Co-concentrations (in ppm). **Lithology and concentration legends from (a),**

(b) and (c) are also used in (d), (e) and (f). [Ab = Albite, Act = Actinolite, Bt = Biotite, Chl = Chlorite, Kf = K-Feldspar, Ser = Sericite].

Lines 623–624:

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: From the data discussed, Pyrite A has a 'lighter' (lower) max δ34S (+5.9‰) than pyrite B (+7.3‰) or pyrite c (+7.4‰). This therefore does not constitute "the heaviest δ34S signatures". This statement needs to be changed. Also, use higher/lower, rather than lighter/heavier when discussing δ34S values.

Response: Rephrased to: 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).

Lines 787–789:

Although a careful data checking of LA-ICP-MS ablation profiles for possible ablated inclusions was carried out, the presence of nanoparticles containing portions of trace elements should not be excluded (Cook et al., 2009).

RC: What is the spatial resolution of the LA-ICP-MS analysis that was conducted? This would provide an approximate value for which the potential nanoparticles would be smaller, if present.

Response: With a spot size of 40 micron, a 5Hz repetition rate, an ablation rate of 0.5micron per second and a scanning speed in the order of 0.2s across the mass range, an inclusion of about 1 micron represent a volume of 0.06% of the total ablated mass, so we will not be able to see nanometer inclusions.

Line 805:

In addition, the Se/S ratios of this pyrite type display a much wider scattering (and a higher mean value (compared to pyrite A .

RC: As mentioned earlier in the text, the Se/S ratios for pyrite C are similarly wide ranging, so using mean Se/S for a comparison between Pyrites A and C is misleading.

Response: Sentence is misleading and is removed.

Lines 816–879:

Section 5.5 Implications for mineral exploration

RC: Much of this section is repetition of previous sections with limited further discussion. Re-write and distil this section down to key points regarding the "Implications for mineral exploration". Lists of positive and negative PC loadings of elements are not warranted here.

Response: Following this suggestion, the sections 5.5 and 6 are merged and shortened to section 6. Conclusions and implications to mineral exploration.

Lines 865–879:

RC: Given the overlapping ranges of δ34S in all the pyrite types, it should be stated that sulphur isotopes are not a distinguishing factor between different pyrite generations (and thus mineralization zones).

Response: Following the suggestion of the review, the following was included in the rephrased section 5.4 Signatures of sulfur isotopes in pyrite and ore-forming processes: The overall $\delta^{34}S_{VCDT}$ data of pyrite grains at Raja are between -1.8 ‰ and +7.4 ‰, covering a common range of sulfur isotope composition for orogenic gold deposits (Molnár et al., 2016a). Considering the similarities of $\delta^{34}S_{VCDT}$ values in each pyrite type, these signatures are not diagnostic, but rather indicative of anomalous Co- or Au-zones. However, the combined use of trace element geochemistry and S-isotopic signatures in pyrite can help to discuss the behavior of S, hydrothermal processes, fluid/rock interactions and accumulation of metals during the formation of the Raja Au-Co prospect.

Line 885:

The LA-ICP-MS study of sulfides, specifically the ubiquitously present pyrite, offers a high spatial resolution and a novel approach in the determination of vectors to ore.

RC: As mentioned before, you have not utilised the high spatial resolution of LA-ICPMS in this study by assessing the variation in trace element concentrations between pyrite rims and cores. You have averaged out the elemental concentrations within each pyrite, potentially missing important evidence for the timing of mineralizing fluids. I suggest revisiting this data, where feasible.

Response: The reviewer is correct with the statement that in the evaluation of the large-scale picture the focus is mostly put on the averaged data from texturally distinct pyrite B.

However, when looking at each data point regarding the data point position within the grains, the core-rim variations showed a very erratic behavior that did not allow any systematic categorization or a general establishment of a core-rim trend. This, however, is what is to be expected when the variation is related to variable redox conditions, or fluid mixing in a dynamic system (where the actual value is depending on the variable masses of mixing fluids). Regarding the more detailed study of this pyrite type, the reviewer is correct with the statement. However, the aim of this study was to find endmembers that could provide potential vectors to exploration targeting, which is why more focus was put on the two endmember pyrite types.

Lines 880 onwards:

RC: Much of this section is repetition and/or unnecessary statements regarding the purpose of the study. Please rework this section to be more succinct.

Response: Following this suggestion, the sections 5.5 and 6 are merged and shortened to section 6. Conclusions and implications to mineral exploration.

Lines 893–897:

RC: These statements/ore formation models should be made explicitly in the discussion section and summarized in the conclusions. Ore-formation models should not be first proposed in the conclusions.

Response: Following the suggestion of the reviewer, these statements were included in the rephrased section 5.4 Signatures of sulfur isotopes in pyrite and ore-forming processes.

Please also note the supplement to this comment:
https://se.copernicus.org/preprints/se-2021-119/se-2021-119-AC2-supplement.pdf