Vectors to ore in replacive VMS deposits of the northern Iberian Pyrite Belt: mineral zoning, whole rock geochemistry, and use of portable XRF

The paper entitled "Vectors to ore in replacive VMS deposits of the northern Iberian Pyrite Belt: mineral zoning, whole rock geochemistry, and use of portable XRF" presents mineralogical and bulk geochemical datasets from the Aguas Tenidas VMS deposit in the Iberian Pyrite Belt. The study focuses on the application of trace metal ratios and concentrations in bulk-rock powders to the discovery of VMS mineralisation. In addition to this the study compares data obtained from whole-rock (ICP + XRF) data with portable XRF analysis. The latter in my opinion is very important and gives the paper a clear application to the mining and mineral exploration sector. In parts I found the structure confusing and think it needs to be more clearly separated into proximal and distal facies in terms of both mineralogy and geochemistry. I struggled to link the core and core location to the geochemical data. To overcome this, I suggest including representative core photos and more logs like those included in Figure 11. Generally there was a lack of quantification throughout with terms such as "hot", "proximal", "slight" or "laboratory" but no explanation/quantification was given as to what these terms specifically meant. Clearly there is an interesting story here but the manuscript was very long and unclear in some areas. At the moment I think the key points are lost in amongst extraneous information which makes the paper confusing to read.

Please see my detailed comments below:

Line 1: Title, consider "replacement style" instead of "replacive"

Line 3: Do not abbreviate XRF in the title, spell it out.

Line 9: I would not state mineral systems – I think ore deposits or economic mineralisation would be more appropriate. Mineral systems gives the impression of mineralogy or mineral-scale chemistry.

Line 10: Define what you mean by "vectors to ore" – geochemical, mineralogical, other or both?

Line 11: suggest swapping "outstanding" for "world-class"

Line 21: What does XRF stand for?

Line 31: I question this statement as the analytical spot size of a pXRF is a few microns (?). What if you have coarse mineral grains? The mineral scale partitioning of different elements between minerals will be important and severely bias your data.

General comment, throughout I suggest change "replacive" to replacement type.

Line 40: Under covering? Are you referring to increased overburden or simply that we are having to hunt in hard to reach places such as tundra and rainforests? Please clarify.

Figure 1: Nice figure, some labels such as CCPI need to be explained. What do the two black dashed lines represent?

Line 62: Give an approximate tonnage, see Galley et al., 2007 (I think their figure is >1.5 Bt of sulfide ore).

Line 83: What do you mean by mineralogical zoning? Alteration halo?

Line 92: Define “hot” and I suggest replacing with “high temperature” ~350°C

Line 92: ambient → surrounding

Line 93: feeder zone… that directly underlies the massive sulfide mound

Line 93: You keep mentioning replacement, you should add a sentence explaining exactly what you mean by this and how this differs from the typical exhalative VMS deposit model.

Line 103: I would separate this into hypogene mineralizing processes and then anything that is secondary in origin – why are the secondary processes important? Because they can modify the primary signatures.

Line 108: remove “related to”

Line 116: You state a tonnage for La Zarza why not for Neves Corvo etc.?

Line 119: Specify an age next to the geological time periods, this would be easier for the reader to understand.

Lien 130: oldest to youngest.

Line 133: Chemical sediments? Please specify a rock type.

Line 134: I would insert a reference back to Fig. 2 here as you are discussing the location of the deposit.

Line 141: very minor point… comma is missing after “et al.” on Velasco-Acebes et al. 2019 (and some other reference throughout).

Line 148: Is there an approximate temperature range for this? Or at least specify the upper temperature limit if possible. Green schist should be one word.

Line 151: Use of “ores”, are they actually ores, do they have an economic value?

Lien 151: This should be integrated with above paragraph or deleted – it seems a little out of place.

Line 155: “The” Agus Tenidas deposit

Line 160: Could you state an approximate depth of burial/overburden?

Line 161: Be consistent, is it W or west?

Line 176: (Figure 3) I would instead say aerial view or plan view and cross section view looking (X direction). You should also state what the black lines are, it’s obvious to me that they are drill holes (I hope!) but this should be stated.

Line 183: Delete “at large”

Line 190: In what quantity are these minerals present? Presumably trace amounts <1%?

Line 193: Avoid 1 sentence paragraphs, integrate with above paragraph.

Line 197: Replace “material” with lithologies.

Line 201: Dismembered by tectonics? Do you mean faulting during later tectonic events?

Line 208: add “The” to the beginning of the sentence.

Line 213: What do you mean when saying “strong vertical and lateral facies changes”? Please specify, for example, in my mind I think of grain size or rock type, is that correct?

Table 1: Do not abbreviate unit to U in the table – if you write unit than you can delete the name you repeat in the brackets below and just include the abbreviation – this would make the table clearer.

In the table you use terms like “rich” and “less” can these be quantified?

Line 223: Other deposits, such as?

Line 227: Earlier in the MS (Line 148) you state up to greenschist facies metamorphism

Line 228: Remobilisation of what?

Line 230-231: I would deleted this, you state this is more detail in section 3.1, no need to repeat.

Line 239: Don’t start a sentence/paragraph with an abbreviation, spell it out. When you say “whole rock analysis” what does this mean?

Line 242: Is there a document provided by SGS outlining the detailed methodology? If so, this should be reference here.

Table 2:

MU5 – define “close to MU-2”

In general I found the table hard to follow. This should be moved to the appendix, instead why not include some representative core photographs? I think it would be more useful for the reader to visualise what the core looks like. Core logs for key boreholes as well perhaps.

Figure 6: Referring back to Fig. 3 for the legend is not appropriate, this needs to be included in this figure.

Line 251: A selection of samples, n =?

Line 252: GOLDD Technology? I have no idea what this means, delete or specify.

Line 266: Avoid 1 sentence paragraphs… integrate with above section.

Line 273: You mention that it confirms their observations but you need to state what these observations are.

Line 276: What does distal mean? 10 m or 10 km, this is important and not clear to me.

Line 277: But the rocks surrounding the deposit have also been exposed to prehnite-pumpellyite facies metamorphism so they don’t only preserve seafloor metasomatism.

Line 283: Change “mafic crystals” to igneous glass or groundmass.

Line 287: You say that sericite-quartz alteration dominates? Is this not a function of host rock, i.e., you might have a higher proportion of felsic lithologies in these drillcore samples?

Line 299: add zone after hydrothermal alteration.

Line 310: “Minor to rare”, this is subjective and should be quantified – <5 vol.%?

Line 311 and 313: Specify units for the depth measurements, presumably m.

Figure 7: petrographic microscope picture → photomicrographs

Again add units after measurements (m) – nice images!

Line 334: reference to Fig 7H that shows Fe oxides (?)

To make section 3.1 easier to understand I suggest sub-dividing it into proximal and distal sections and hangingwall and footwall. It becomes confusing when swapping between different drill holes and you easily lose the reader.

Line 365: Yes, I agree that hyperspectral imaging is great for exploration but you focus on drillcore samples, how is this method applicable to your data/deposit? I would summarise your key alteration findings here (i.e. the expected spectral response of proximal vs. distal alteration) and relate this to hyperspectral imaging.

Line 370: Unit → rock, also extra e on halos.

Line 373: I don’t think mineralization related lithologies is what you are identifying, rather it is chemical changes that related to specific hydrothermal/mineralising events.

Line 374 are “to ore deposits” after pathfinder

Figure 8: In the text you reference figure 8b – A and B are missing on the figure.

Figure 9: Why are you plotting sedimentary rocks on this diagram (i.e. the black plus signs)? Maybe I’m missing something but I don’t understand why plotting sedimentary rocks on this diagram is useful.

Line 423: By definition lavas are not intrusive therefore you erupt and not intrude a lava.

Line 438: Not the discrimination diagrams themselves, rather the use of immobile element ratios.

Line 452-453: rhyolites A-X does not mean anything to the reader, simply state that they are from different rhyolite units.

Line 468: List some examples of common mobile elements.

Line 480: Are you saying albitisation, chlorite and sericite are produced during distal seafloor alteration? Chlorite is a high T mineral (>300°C), ambient seafloor alteration typically forms smectite with Fe-oxides and maybe minor zeolite minerals. Please clarify if this is seafloor alteration or if its related to later metamorphism.

Line 482: little → minor

Figure 10: As per my previous comment, please include a key in each figure. Why not add fields indicating typical proximal or distal facies or arrows from proximal to distal in AI-CCP space?

Line 512: higher → upper portion

Line 526: ΔC_{i-}– what is this? You do this in the next line but the explanation should come first.

Figure11: I think these type of drillcore log figures should be included earlier along with core images for context. Units missing on Y axis. What are the little black lines with arrows? Faults presumably – please state.

Line 548: Why are they deep fluids? Why not just high temperature?

Line 556: How enriched? Give a value.

Line 577: Replace either broadly or broader, repetition.

Line 586: Saying “later stage” is misleading as this still formed on the seafloor – in fact from active SMS deposits some studies suggest the addition of Si very early (You and Bickle, 1998, Nature).

Line 590: delete “characteristic”

Line 618: Example of elements that are used is needed.

Line 619: Define behavior of the element? Presumably you are referring to its solubility which is controlled by temperature, Fo2 and pH.

Line 622: I’m not sure this statement is correct – there are many issues associated with Tl and Hg, especially when using whole rock digestion methods as they are highly volatile. Moreover, Sb generally occurs at very low concentrations.

Line 659: Geochemically anomalous envelope of what? State which elements are anomalous.

Line 682: But why are Sb and Tl below detection? Something to do with temperature perhaps?

Line 701: Or that these elements were not present in the first place.

Line 713: I would present argument 1 and 2 and then discuss why you favour one over the other, in other words, remove the section “in which case…”

Line 729: This section is unclear to me, I’m left wondering what argument you favour? Please clarify.

Line 731: Indicative trace elements? Which trace elements and indicative of what?

Line 734: Delete into the sea bottom → exhaled at the seafloor

Line 735: I’m sorry, I don’t understand what is being said here. You don’t see an alteration halo above the deposit – but I thought there was a fault zone (later) with displacement so why would you expect to see any halo?

Line 741: Please specify what these indicator elements are, the reader should not have to go back and check.

Line 749: Define proximal, you say 500m in the next line, add it in brackets here.

Line 757: Why do they have to be volatile elements? Why not just elements?

768: Geochemical alteration halos in… VMS deposits in the IPB fall…

Line 771: Define “high transportation temperatures” – generally >280°C

Line 784/785: Delete this sentence, you do not discuss Rb or Sr so don’t include this.

Line 788: And lower detection limits.

Line 794: Hollis et al., 2021 in Minerals is also a good VMS reference to add.

Lin 806-811: This describes the figure and should be re-located to the figure caption.

Line 820: But aren’t you analysing powders that *should* be homogenous? Nice point to show that you need X amount of analysis to replicate bulk sample concentrations.

Line 826: But surely the grain size of different mineral is far more important? For example analysing a granite would be no good as the individual minerals are very coarse vs. a shale which is fine grained.

Line 830: Unreasonably high values → unreasonably high concentrations relative to whole rock values.

Line 854: Is Myra Falls a VMS deposit? Please specify.

Figure 14: What do the grey dashed boxes represent? In the caption you state “laboratory”, what method does thus follow? Is it ICP or desktop XRF.

Figure 15: Again specify what is meant by laboratory – I think these plots are very useful.

Line 876: Define what you mean when you say “nugget effect” I would not think the nugget effect applies to an element such as Zn, are you referring to the analyses of mineral inclusions?

Line 901: Discriminant → discrimination

Line 944: The biggest issue I see with this statement is that there is no consideration given to mineral grain size – i.e. a coarse vs fine grained rock. I think this would have a profound effect on the data collected, and, as you demonstrate, different elements partition into different minerals, this would cause a serious bias in the results.

In general I think this study should be simplified and the discussion sub-divided into clear topics, maybe, proximal and distal alteration at first and then afterwards into sericite, albite, chlorite (etc.). You could then go on to compare with other VMS deposits. This would make it easier to follow where you are in relation to the ore deposit. The addition of representative drill core samples is essential and will provide much needed complex. The title of the manuscript mentions the use of pXRF but this is currently underrepresented in the text, including some of the figures that are currently in the supplementary information would strengthen this aspect in the manuscript.

Supplementary material: There is a lot of information included in the supplementary material, some of which (such as the logs) could be useful to include in the main text. I also think it would be useful to include the figures such as S3 (section S1.3) in the main text, I think this is great data and is very important when considering the application of pXRF data in industry.