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## Revisions and Response Letter MS No.: egusphere-2022-825

Dear Dr. Di Muro,

please find attached a revised manuscript entitled "Spectral characterisation of hydrothermal alteration associated with sediment-hosted Cu-Ag mineralisation in the Central European Kupferschiefer", co-authored by Léa Géring, Moritz Kirsch, Samuel Thiele, Andréa De Lima Ribeiro, Richard Gloaguen, and Jens Gutzmer, for publication in EGU sphere. This manuscript has not been published, nor has it been submitted elsewhere. The original manuscript was subject to revisions. We thank you and the reviewer for the opportunity to further increase the clarity of our manuscript. We outline our actions in point-by-point form below.

As we stated in our previous cover letter, we feel that the content of this submission is directly applicable to scientists working with hyperspectral data sets and thus would be of interest to the wide constituency of readers of EGU sphere. This contribution focuses on what additional mineralogical information can be provided from drill core hyperspectral data to logging work in the context of kupferschiefer exploration. Data were captured in visible, near, shortwave, midwave and longwave infrared what allowed cross validation between the different IR domains. We identified shortcomings inherent to the technique, like overlappings, or the fact sulfides ore has no spectral signature, neither as organic matter. Some alteration mineral's spectral signatures could be observed, and their characteristic were investigated regarding relevance for exploration of Kupferschiefer-type deposits.

We thank you for your consideration and look forward to hearing from you.

Yours sincerely,  
Léa Géring et al.

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## **ACTION ON REVIEWERS' COMMENTS (POINT-BY-POINT RESPONSES)**

### **Comments by 1st reviewer (Gregor Borg):**

A minor annotation for the entire manuscript: Use “s” (English spelling) instead of “z” (American English spelling). European Authors publish in a European Journal – unless the editors insist on American English spelling.

Revised.

Line 40-41: *The figures given by Kopp et al 2012 are predominantly based on historical data. The spacing of the bore holes (including the very few ones added by KSL) do not fulfil current international reporting requirements to delineate proven, indicated, or inferred reserves. Please add a sentence such as: “These are mainly historical resource figures and do not comply with current international reporting regulations, e.g. to the JORC or NI43-101 codes.” Your paper is very strong based on your own research and will be used and quoted abundantly, you would not want to raise an interest in The Spremberg Kupferschiefer for the wrong reasons*

We agree that there is a need to emphasise that the calculation of the resources is historical and does not reflect the methods for calculation used today. We added the sentence recommended by the reviewer.

Line 80: replace “lithologies” by “lithotypes”. Lithology (the logos of the lithos), is the overall science of the rocks, Lithotypes are various rock types or rock sequences, of which there can be many.

Revised.

82: “Lower” instead of “lower” – stratigraphic term, change throughout the ms

Revised.

99-100: *I personally think that subduction-zone-related lithotypes in shear zones in the Mid-European Crystalline High have also contributed to the mineralisation. The spatial coincidence of the Kupferschiefer ore bodies with the arcuate-shaped MECH is simply too striking. You might add behind “infill” a small insert like “and possibly from sheared and faulted basement rocks”.*

As shown in figure 11, we agree that the basement-derived hydrothermal fluid contributes to the Kupferschiefer system. Hence, we modified the text per the suggestion of the reviewer.

110: You should mention and cite Symons et al. (2010) who have dated the hematitic redox-front at Sangerhausen with two palaeomagnetic ages (149 Ma and 51 Ma).

We added a sentence: “The hematitic redox front in the mineralised shales was dated at 149±3 Ma and 53±3 Ma using palaeomagnetic techniques.”

118: better “that is of Cretaceous age”

Revised.

141: “well-mineralised” instead of “well mineralised” – check ms throughout there is inconsistent use of the hyphenisation

Revised.

143: “comprises Cu ...” rather than “comprises of ...”. N.b. “coprises x, y,z” but “consists of x, y, z”

Revised.

214: “These ...” not clear what “These” refers to – please rephrase

We corrected the text, replacing “These” by “The drill cores”.

216: “comprises of” see my comment above and check entire ms for same error

Revised.

219: Replace “Owing to” by “Due to”

Revised.

225: Replace “hasn’t” by “has not”, n.b. the former is not used in written English

We corrected the text.

385-390: *Interesting observation. You might want to consider the decomposition and replacement of feldspar as a probable source of the kaolinite. The replacement has been documented from lithic clasts in the Grauliegend in Hessen, where the feldspar component has been replaced by chalcocite and chalcopyrite, probably producing kaolinite and silicification (from the excess Si) either proximally or distally (Borg et al. 2012 and other papers, e.g. in “grey” literature such as World of Mining). The hand specimen is part of my private collection, can be made available and could be used for hyperspectral scanning as a nice separate exercise* ☐

We also think the kaolinisation of feldspars is the source of kaolinite and that this probably happened under weathering of the rocks by hydrothermal fluids that also supply copper. Thank you very much for your reference/comment that confirms our thought. We also mention Minz’s (2011) petrographic analysis in this regard since she observed that kaolinite seems to be cogenetic with Cu-Ag mineralisation.

397: “discoloured” means void of colour, e.g. bleaching. “coloured red” or “reddened” would be the more appropriate term.

Revised.

*Comment on hematite redox colours in general. Scientists with a lot of experience in the colours of the Rotliegend (lighter red with a slight orange hue) and Rote Fäule (slightly darker and more violet) insist that they can distinguish the red colours between both. It would be very interesting to know how your spectral measurements distinguish these two (or more reddish colours). You state that you cannot distinguish, ok, but this might be worth to follow up on later.*

Because of the lack of material analysed, we could not conduct a systematic analysis of distinguishing the Rotliegend from the Rote Fäule. As suggested by the reviewer, we may conduct further analysis of this interesting aspect in a follow-up study.

421: “toward shallower level” ? do you mean “towards a shallower level) or “towards shallower levels”? please correct

Corrected. We meant “towards shallower levels”.

429: as mentioned before, check for “s” and “z”. Here you (correctly) use “s” in “mineralisation” - check throughout ms

Corrected.

464: you might want to insert after “(Kl)” “, possibly at the expense of feldspar that has locally been partly decomposed.” But check for such features.

We thank you for your suggestion and revised the text accordingly to: “This observation is consistent with an interpretation of the kaolinite as a hydrothermal alteration mineral, *possibly formed at the expense of feldspar that has locally been decomposed*, and suggests that Kl could also be used to track high-temperature fluid flow within the sandstone.”

### **Comments by 2nd reviewer (Andrea Di Muro):**

The research paper « Spectral Characterisation of hydrothermal alteration associated with sediment-hosted Cu-Ag mineralisation in the Central European Kupferschiefer » submitted by Gering and co-authors represents an interesting test of the contribution of hyperspectral imaging on drill cores for their mineralogical characterisation.

The test consists in the identification of the spatial distribution in the drill cores of spectral indices, whose interpretation is based on independent studies and calibrations.

Discrepancies (ex fig. 6b) with respect to interpretations proposed in the literature are attributed to possible effect of grain size, crystallinity and texture (ex near veins); However, the quite large discrepancy measured for dolomite, for instance, might arise from compositional differences with respect to the reference spectra and mixing between compositional poles occurring in the natural samples.

The carbonate composition in the SWIR is well studied, and our samples show two endmember compositions in this spectral range plotting near the known calcite and dolomite poles, respectively, which suggests limited mixing between calcite and dolomite. In the MWIR and LWIR, the carbonate absorption is scattered between the respective carbonate endmember compositions. However, if plotted against the SWIR, they form two distinct vertical linear arrays (Fig. 7). The spectral variability in the MWIR and LWIR has been interpreted to be due to compositional mixing effects, but also grain size and crystallinity (Zaini et al, 2012). Also, according to infrared and  $\mu$ -XRF maps along cores and on hand-specimen, we concluded that shifts of F11300 seem more texture-related (line 312) or affected by mixture with other non-carbonate minerals.

The authors compare hyperspectral imagery with micro X Ray fluorescence spectrometry to “validate” the alteration minerals. However, chemical mapping does not exactly correspond to a validation of mineral mapping as that would require comparison with independent techniques able to identify the same phases (for instance micro Raman mapping).

We agree that the term “validate” might be wrong in this context. We replaced it with “corroborate” in the text. We interpreted XRF data with a clear idea of the mineralogy of the system based on previous petrographic studies, and used it as a qualitative validation of the hyperspectrally derived indices. For instance, we knew the Al map would be mainly related to micas, Si to micas and quartz, S

to sulphates and sulphides, Ca and Mg to calcite and dolomite, respectively. We observed that the F3700 and F2330 carbonate spectral indices correlate well with Ca and Mg intensity in the XRF maps, demonstrating that these indices can be used as a proxy for carbonate composition.

The study concludes that very fine grained and carbon-rich units are difficult to analyse and that peak overlap hinders the identification of some phases in some specific lithotypes (ex sulphates in qtz rich sandstones).

The potential shortcomings of the technique identified in this test are not summarized in the abstract and I suggest the authors add this important information in the summary.

We agree that the shortcomings of the techniques should be addressed in the abstract and thus added a corresponding sentence.

#### **Comments by 3rd reviewer (Anonymous)**

The manuscript "Spectral characterization of hydrothermal alteration associated with sediment-hosted Cu-Ag mineralization in the Central European Kupferschiefer" analyzes drill cores using hyperspectral imagery in various wavelength domains. The authors characterize spectral features and compute spectral indices to derive the mineralogy of drill cores. Additionally, Micro-X-ray fluorescence measurements are taken in order to cross-check the results from hyperspectral imagery analysis. The authors identify a number of minerals, and they use the derived mineralogical information to infer characteristics of alteration processes and qualities of geological formations that are relevant to better understanding the Cu-Ag mineralization in Kupferschiefer-type mineral systems.

The manuscript is overall well-written. The figures and tables are mostly clear and helps in the understanding of the manuscript. The organization of the manuscript is also clear.

The main comment for the manuscript is the justification to use hyperspectral imaging in VNIR, SWIR, MWIR, and LWIR for all drill cores which seems excessive. Hyperspectral imaging of multiple drill cores using four cameras with high spatial resolution leads to a large amount of data. In order to analyze minerals discussed in the manuscript, not all of this functionality is necessary, and likely, the useability of data is not optimal while needing a large data storage space and long measurement/analysis time.

We agree that the acquisition time and storage space are slightly increased, but the combination of VNIR, SWIR and LWIR is essential to constrain many mineral assemblages with accuracy. The benefits clearly overcome the suggested disadvantages (e.g. larger data). In the present study the combination of sensors is beneficial for three main reasons (which are mentioned in the text, e.g. lines 536, 524):

- Each of these infrared domains allows analysis of different minerals that are of importance in the Kupferschiefer: VNIR is useful for the discrimination of iron oxides, SWIR for clays and carbonates and LWIR/MWIR for silicates (quartz and micas).
- A broad range of infrared provides a means to check if features are associated with one single mineral or a mixture. While pure minerals

can be identified with a limited spectral range, disentangling mixtures often requires multiple diagnostic features and hence an extended spectral range.

- Multiple spectral ranges enable cross-validation, particularly for minerals that show absorption features in different spectral ranges. The position and intensity of absorptions/emissions for a particular mineral in different spectral ranges could potentially also provide complementary information regarding composition, grain size and crystallinity (e.g. in carbonates)

A similar and sufficient information can likely be retrieved from point or line measurements, such as with spectroradiometers, rather than full images. In fact, mineral index maps of drill cores in figures 5, 8, 9, 10, 11, 12, and appendix 1 show that the variation in the width (short side) direction of the drill cores is small. It is the length (long side) direction that the variation is the highest and the most informative for analysis. Therefore, acquiring images does not appear to be an optimal method and mostly leads to increase in redundant data not critical for drill core analysis. The authors could have taken images of one or two cores as representative trials, then moved on to simpler point/line measurements for other cores. Alternatively, the authors could have decided to use only a subset of cameras based on prior information or information made available with the initial scan of the first camera. There may be other data acquisition methods that could have led to better optimization. An improved justification for the need to acquire full imagery in all 4 wavelength domains on each drill core over point/line measurements or a select wavelength domain is needed.

We are aware of the fact that hyperspectral line sensors are deployed in the industry as a cost-efficient solution. However, in the framework of this scientific study, and particularly with large diameter (ca. 10 cm) drill cores such as the ones used in this study, we argue that:

- imaging systems sample a larger area and so are statistically more reliable / less prone to, e.g., orientation biases than point or line measurements
- they can resolve structures such as veins, nodules and alteration halos much better, along with RGB (and false-colour) image representations that facilitate interpretation (e.g. Figs. 9, 12)
- most of the time/effort during drill core scanning goes into preparing core trays and setting up equipment, so imaging systems are equivalent in efficiency to line scanning systems (albeit with potentially higher initial costs for the equipment itself). Processing image data requires more computing power, but this is more than achievable on even relatively modest computing infrastructure.
- they allow a better correlation/comparison with automated mineralogical information, such as MLA or QEMSCAN, that leads to more accurate mineralogical estimations (although this is beyond the scope of the current study).

Line 11 – 12: Hyperspectral imaging permits the rapid, cost-efficient and continuous characterization of alteration mineralogy and texture along entire drill cores with a spatial sampling of a few millimetres.” This may be an overstatement, particularly “rapid” and “cost-efficient.” It could be true in comparison to other methods, though that is not mentioned. As mentioned in the comment above, drill cores often show major variations in one dimension and the second dimension is often not informative where a continuous point or

line measurements could be sufficient rather than full imagery. Hyperspectral imaging may not be necessary in this case, and it is rather more reasonable to use for imaging objects with larger areas, like outcrops.

See our answer to the previous comment. We agree that this method can only be rapid with well-developed pre-processing workflows. However, the processing methods that we used to map mineral indexes here give continuous information for several metres of drill core in minutes, so it is much faster than logging and gives the added benefit of objective and quantitative data that can be re-interpreted or integrated into logging workflows. Critically, it also provides additional information like carbonate rocks composition (calcite vs. dolomite), and helps to identify and quantify hydrothermal alteration phenomena (e.g., hydrothermal hematite and kaolinite) that may be inconspicuous to the naked eye.

The hyperspectral drill core scanner with all four sensors is certainly a monetary investment but likely quickly compensated by the return value of facilitating automatic geological logging and replacing the need for extensive chemical assaying and sample-based mineralogical analysis. Finally, as mentioned in our response to the previous comment, the acquisition time required for imaging and linear hyperspectral data is comparable, as the majority of the time investment is spent preparing cores for scanning, regardless of the technique applied.

Line 16 – 17: Please specify the wavelength ranges of visible, near, shortwave, mid-wave and long-wave infrared.

We added this information to the abstract.

Line 50: Please specify again the wavelength ranges for each wavelength domain.

In the main part of the manuscript, the ranges are specified in Table 1.

Section 2.1: As the calibration of the VNIR-SWIR measurements are explained using grey panel, please also explain the calibration of MWIR and LWIR measurements. Currently, the only information available is the last row of Table 1 which is not enough. Also, please specify if the MWIR and LWIR measurements are reflectance or emissivity (Figure 6a suggests reflectance).

All measurements presented are in reflectance. The calibration of the MWIR and LWIR measurements is achieved using a diffuse aluminium panel. We added this information to the text and corresponding table.

Line 361: I believe “is” is not necessary in “... local enrichment of mica in the dolostone is found directly above the mineralized zone ...”

Corrected.

Line 362: Insert “and” before “this is confirmed by ...”

Revised.

Figure 12b,d: Explanation is needed regarding why the absolute reflectance and pattern are not consistent in figures 12a and 12b where the wavelengths overlap. Some discrepancy in absolute reflectance is expected when materials

are observed in different cameras, but the discrepancy in this figure appears to be excessive. It is reasonable to think that, based on Figure 12b, at least the Fe-rich dolomite spectrum to be lower than the dolomite spectrum in the wavelengths near 800nm in Figure 12d. If there are calibration discussion of the instruments, please elaborate in the Methods section.

We thank the reviewer for spotting this apparent inconsistency which was due to unclear labelling. The spectra in subfigures (b) and (d) actually come from different rocks. We have revised the figure for improved clarity.

Section 4.2: The overall tone of this section seems overly optimistic regarding the application of hyperspectral imagery to drill core analysis which might be arising from the lack of discussion of the limitations. As mentioned, imagery may not be always necessary, and four wavelength domains may not be always necessary. Addition of discussion of alternative, more targeted approaches may benefit this section. As the authors mention, the Kupferschiefer itself was difficult to characterize using hyperspectral imagery, thus a discussion of using hyperspectral data in conjunction with other types of data may also benefit.

Please refer to our previous responses regarding the relative benefits of image data vs. point/line measurements and the four wavelength domains used. We have added shortcomings of the hyperspectral analysis, such as mineral features overlap and low reflectance of organic-rich, fine-grained rocks to the abstract to explicitly point limitations out to the reader. In the manuscript, we state that hyperspectral data can be used in support of methods that provide semi-continuous information along cores, such as sample-based geochemical or mineralogical data. Lastly, we certainly do not imply that HSI should be the only data type acquired during core analyses; integration of diverse data is always important.

Appendix 1: The figure is too small, especially the text.

Revised.