Biogeosciences Discussions

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Reply on RC1

Gerhard Franz et al.

Author comment on "Fossilization of Precambrian microfossils in the Volyn pegmatite, Ukraine" by Gerhard Franz et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-332-AC1, 2022

Authors' comments to Fossilization of Precambrian microfossils in the Volyn pegmatite,

Ukraine, Gerhard Franz et al., Biogeosciences Discuss.

We thank both reviewers for their careful reading and their comments; all comments are very helpful to improve the presentation of our results!

Reviewer 1 SPECIFIC COMMENTS

Line 63 – says high N-content is typical for the OM, but Line 33 describes loss of N (and S) due to anaerobic oxidation. Please clarify. Is the N content low from oxidation, but still high enough to be "typical" for OM?

Yes, the N content of the less mineralized OM is in the order of 8 atom%, that of strongly decayed OM is 2-4 atom%, which is considered as typical and high.

Line 83 – refers to "long cooling history" – is there an estimate on what amount of time is considered "long" (thousands of years? millions?); or at what depth this cooling might have occurred (meters?)

The intrusion depth is considered as 2-3 km; after the intrusion of the pegmatites (1,760 Ma) there is a well-documented intrusion event nearby with ages of 1.758 Ma, the lowest age with 1.743 Ma, which shows that at least for two million years, possibly 20 million years there was igneous activity. The large diameter of this part of the pluton (approximately 60 km) and the whole pluton (>120 km) clearly points to a long cooling history, in the order of millions of years.

Line 93 – OM is referred to as "highly mature" based on pyrolysis and TEM results. What about these results indicates the OM is highly mature? This sentence could also be moved to the results or discussion section where these findings are covered in more detail.

We agree to move the sentence to the results section. There we will argue: All are strongly dominated by hydrocarbon gases C_{1-5} (methane through pentane) and subordinately by alkylated mono- and diaromatic compounds. These are typical pyrolysis breakdown products of organic matter in general, but as higher n-alkyl homologues (n-C_{6+}) or oxygen-, sulphur-, and nitrogen-functionalized compounds (e.g., phenols, thiophenes, and carbazoles) as indicators of biological precursor structures (Larter, 1984; Horsfield, 1989; Sinninghe Damsté et al., 1989) are essentially absent they are indicative of mature OM. Loss of functional groups during diagenesis and loss of H-rich components during catagenesis leads all organic matter types to move towards the point (metagenesis) where they become indistinguishable finally possessing only a potential for the generation of dry gas (methane) and mono aromatic compounds (Tissot and Welte, 1984; Quigley and Mackenzie, 1988; England and Mackenzie, 1989; Horsfield, 1989). In line with a remaining fluorescence the composition of the pyrolysate, especially presence of wet gases (C_{2-5}) and diaromatic compounds, indicates that the OM has not yet arrived at metagenesis (R_o>2.0%, where R_o = vitrinite reflectance in oil (Tissot and Welte, 1978). GC-fingerprints resemble e.g. those of Paleozoic coals and shales from Australia at 1.7%< R_o <2.3% (Figure C2 in Mahlstedt et al. (2015) and Figure A2 in Mahlstedt et al. (2014). Assuming typical geological heating rates between 1 and 3K/Myr and based on the easyR_o model (Burnham and Sweeney, 1989) OM at these maturity levels must have been heated to somewhere between 175 and 200°C.

Line 95 – "partly failed" – how did the Pb analyses partly fail? It is unclear here, please expand.

We propose to write more explicitly: Attempts to directly date black opal with inclusions of OM and of filamentous kerite using U-Pb-systematics resulted, in the case of opal, in scattered U-Pb data indicative of open system behavior. For the filamentous kerite we obtained a nominally Cambrian minimum age that is consistent with the inferred Precambrian age.

Line 108 – "sampled in situ from the pegmatites" – how was the kerite (OM) sampled? Is it free from other minerals to be collected by itself? Or did it need to be extracted from the host rock? In other words, were the minerals/crystals collected with OM present (as is the case for beryl in the next sentence, Line 109)? (see comment for Line 122 below).

Line 122 – Similar to above comment, it's unclear how the OM was recovered. Was OM extracted from host rock/minerals using acid digestion? If not, please clarify how the OM (kerite fibers) was isolated. (see also Line 207)

The microfossils are found free on the surface or partly in the upper layer of clay on the floor of the miarolitic open "chamber". It occurs there in masses of kg as described in the Russian and Ukrainian literature (Zmuhr 2003, Gorlenko et al. 2000, and references in these papers), as verified by coauthor Chernousenko. It can be found also on the surface of beryl and topaz crystals. So, there is no need to extract it from the rocks with any dissolution process or mechanical separation. This is exceptional for this type of occurrence, i.e. giant open crystal pocket (crystal cave), where the organisms grew.

Line 148 – "using a Parr-type hydrothermal digestion vessel" – Has this technique been applied previously to similar samples? If so, please provide citation(s).

using a Parr-type hydrothermal digestion vessel, a procedure that has been shown to effectively mineralize a broad range of organic matter (Tahán et al. 1993).

Reference: Tahán, J. E., Granadillo, V. A., Sánchez, J. M., Cubillán, H. S., & Romero, R. A. (1993). Mineralization of biological materials prior to determination of total mercury by cold vapour atomic absorption spectrometry. Journal of Analytical Atomic Spectrometry, 8(7), 1005-1010.

Line 162 – "a variable diameter, from 1-2 μm up to c. 80 μm, mostly near c. 15-20 μm." – This is quite a large range of diameters. Please explain. For example, are these observed diameters considered to be from different fossil taxa? Many (most?) modern cyanobacteria exhibit a more limited range of cellular diameters.

As stated in the manuscript, we still have to do more systematical research on the morphological characteristics to speculate about the types of organisms. Most likely there are several taxa, and many of the fibers/filaments resemble modern fungi; however, fungi are heterotroph and require other organic matter. We stated in the manuscript that especially the spherical objects (which are rare, however) will give important hints to the type of organisms, but our data base is still not good enough; this is work in progress.

We had decided to present the data set about the fossilization process first; it is already a large manuscript, requiring a lot of figures, and in order to have good arguments for the type of fossils, this will require many additional figures. In addition, to describe the original morphology of the fossils it is necessary to distinguish features, which are due to the fossilization process.

Figure 2 –

1) Are all of these examples of OM considered "kerite"? Or is it only the "fibrous" specimens? Please clarify (in caption or main text).

2) Samples d–f (and underlying "fiber" on b) seem that they could be classified as "filamentous". Is there a reason for the fibrous vs. filamentous identification? If so, please explain in caption and/or main text.

3) Branched fibers (or filaments) as in "2d" should be discussed. Some cyanobacteria (and other microbes?) are known to occasionally exhibit branched morphologies. Please expand on the significance of branched vs. unbranched morphology (in main text).

Yes, kerite describes the material, highly mature organic matter, something like asphalt, not well-defined, but not restricted to a certain morphology; we will correct this in Table 1. To comment on the branching would already a part of the discussion of the types of fossils, it has nothing to do with the fossilization process (see comment above). However, we can put into the final manuscript some more details (and refer to the previous publication Franz et al. in Amer. Mineral. 2017).

Fiber vs. filament: We will change throughout fiber into filament, fibrous into filamentous, since fiber has a connotation to textile fiber or glass fiber, whereas filament is more common usage for biological matter.

Line 207 and 208 – "handling" and "preparation" How were the fibers handled for preparation? Line 122 describes a lack of physical cleaning or preparation -- please clarify.

The microfossils occur free, there was no need for special preparation. After collection by hand into sample bags, they were strewn (spread) onto the sample holder, mounted with carbon type. The beryl crystals with the filamentous and flaky organic matter were dust-cleaned with compressed air, but no other cleaning process was applied.

Line 208 – To my knowledge, "core-mantel" is not a common terminology for microfossil descriptions. Could this be considered a filamentous "sheath" as observed in some cyanobacteria (as mentioned in Line 446 and 479)? Consider rewording (also "mantle" is apparently mispelled here as "mantel").

The terminology core-mantle is obviously taken from mineralogy; we will change "mantle" into "sheath-like", and core into "central part".

Line 274 – "anaerobic oxidation" – Citation(s) for this interpretation? Does this imply biomineralization played a role in preservation or degradation? Please expand.

An oblique section of a 15 µm-wide fiber (Fig. 7) shows O enriched in the upper right part, where N and S are low, indicating simultaneous N and S loss during progressive maturation of organic matter anaerobic oxidation.

During maturation of organic material labile nitrogen and sulfur-bearing compounds are converted and lost whereas oxygen-bearing macromolecules are enriched (Poetz et al., 2014). Here, mineralization of the organic fraction was preservative due to aromatization and this process caused formation of oxygen-bearing aromatic macromolecules. However, S is low in the area …

Reference:

Poetz, S., Horsfield, B. and Wilkes, H. (2014): Maturity-Driven Generation and Transformation of Acidic Compounds in the Organic-Rich Posidonia Shale as Revealed by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Energy Fuels 28, 4877–4888.

Figure 9 – The elemental distributions of O, S, and N for the botryoidal texture seem to be inverse to other figures (e.g., O and S occur together – possibly indicative of sulfate or other oxidized sulfur?). Please expand.

Line 338 (reviewer means 333) – "thermal overprint" – How is this known to be a thermal overprint? Are there additional indicators for thermal alteration? If so, please explain, or cite relevant literature to help support this interpretation. (See comment for Lines 359 and 360 below.)

We will change "thermal overprint" into "degradation".

Lines 359 and 360 – "These are typical pyrolysis breakdown products of already matured OM." – Please cite other examples of "typical pyrolysis breakdown products" of mature OM, or explain further how this is known.

See comment to line 93!

Line 365 – "between ~175 and ~200 C" – Likely temperatures based on what? Please explain further or cite relevant examples from the literature.

The temperature estimate was derived from mineral equilibria (Franz et al., 2017) and we will put in this comment with the reference.

Line 418 – "Alteration of OM by anaerobic oxidation" – could this not also result from nonbiological oxidation? "Anaerobic" typically implies biological activity; please clarify.

We agree and change "anaerobic oxidation" into "progressive maturation of OM": Alteration of OM by progressive or localized maturation (e.g., the oxygen pattern along interfaces or affecting the whole kerite matrix) as a major feature is also seen in the element mapping (Figs. 7-10).

Lines 446–448 – "their size and transition to botryoidal and dented structures (Fig. 4) is more consistent with an interpretation as a primary feature." – It is unclear how the size and transition to botryoidal/dented is consistent with a "primary" (assumed to be "biological"?) feature. Please explain or cite relevant examples.

Similarly, as in the following comment to lines 459-461, we will reverse the argument: We don't see an easy way that during fossilization the transitional features from ball-shaped outgrowth to botryoidal shapes can be produced. Therefore, a primary = biological feature is more likely.

Lines 459–461 – "the six-sided outline, seen in small and large cavities, cannot be explained by shrinking. There is no reason why a cylindrical body during shrinking should open a central cavity with a regular outline." – I would tend to agree with this interpretation. It is not entirely necessary, but may help to expand on this point. e.g., OM shrinking would not likely result in such uniform shapes, and may be related to mineral precipitation or other fossilization processes.

Lines 595 and 596 – "This is not consistent with our observations" – If the fossils are indeed cyanobacteria, but were not transported from ponds at the surface, how would they be capable of photosynthesizing in the subsurface?

This seems like an important observation and may indicate a different type of filamentous microbial population existing in a continental subsurface environment. Are there other possible microbes (e.g., fibrous/filamentous chemotrophic microorganisms) that could help explain this discrepancy?

Other filamentous microorganisms, which can be mentioned here, are fungi-like organisms. We will include this speculation into the revised version, but cautiously, and will expand on this when have more investigations on the spherically shaped fossils (which could be spores) and about the N- and C stable isotopes.

TECHNICAL CORRECTIONS

Line 25 – omit "own"

Ok

Line 36 – omit "also"

Ok

Lines 39-40 – suggest changing sentence to read, "The geological environment for growth of the microorganisms and fossilization is assumed to be a geyser system,…"

Ok

Line 42 – suggest that the term "caves" should be changed to "large cavities" or something similar. Otherwise, the difference between caves and cavities should be described in the text. Also see other uses of "caves" (Line 609)

Ok; we will introduce in the introduction the description of these miarolitic, large open cavities (in pegmatite terminology often as crystal pocket) and use the term "chamber", which was introduced in the Ukrainian original literature for these (worldwide unique) pegmatites. We will check if we have a good photograph to include into the paper.

Line 43 – suggest changing "prime" to "distinct" or "uncommon" or something similar, in order to differentiate from other descriptions of Precambrian fossils from marine environments.

Ok, we will use "uncommon".

Line 45 – add "preserved in" after "microorganisms", and omit "of". Sentence will then read "… possible habitat for microorganisms preserved in the deep biosphere."

Ok

Line 50 – Propose changing “(meta)sediments” to “(meta)sedimentary rocks”, as Precambrian fossils occur almost exclusively in lithified rocks rather than unconsolidated sediments.

Ok

Line 51 – omit “also”

Ok

Line 51 – provide citations for microbial habitats described from “recent years”

Ok, reference to Ivarsson et al. 2020, a review paper “The fossil record of igneous rocks”.

Line 61 – d13C ratios should refer to values less than negative (–) 40‰.

Ok

Figure 1 – No asterisk (*) on map? There is a black circle where "Volyn" is indicated.

Please change in figure or caption to aid reader comprehension.

Ok, will be corrected.

Line 129 – propose changing “Mappings” to “Maps” throughout (also Lines 340, 449)

Line 124 we will change into “element distribution maps”; however, in the following in some instances the word “mapping” seems more appropriate.

Line 147 – spell out “concentrated”; also, what is the percent composition of HNO_3 (e.g., 68%)?

Yes, 68%.

Figure 2 – (a) annotated arrows would be useful to distinguish fibrous vs flaky, and the background materials (e.g., bladed crystal? in “a”)

Ok, arrows will be put in.

(c) what is the background composed of (behind or beneath the flakes)? It is unclear from the image alone.

Figure 3 – 1) Add arrows to show pores or central cavity in images.

The background is the beryl crystal, and arrows will be put in.

Line 199 – “surface” Surface of what? The fibers or botryoidal shapes? Please cite the EDS spectra referred to here (e.g., Fig. S1)

It says, on line 196, surface of the botryoidal shape; should be clear.

Lines 210 and 211 – Change “analyses 6” to “analysis 6” (“analyses 2 & 5; analyses 3 & 4”)

Which analyses does this refer to? Something in the Supplementary Info? Not sure which analyses are being discussed.

Reference to the Supplement will be put in.

Lines 212 and 213– “count rate for O decreases systematically from outer rim to center” Where is this shown? Please refer to figure.

This is in the same EDS spectra, Supplement; alternatively, we can put these figures into the revised version.

Figure 5 – Line 221 – “central channel” Sometimes this is referred to as the central “cavity”. Suggest choosing one description (channel or cavity) to use throughout, in order to avoid reader confusion.

We will use “central channel” throughout.

Line 225 – “Fiber” It appears there are multiple fibers? Arrows might be useful here.

Indeed, these are two fibers, will be changed.

“numbers” Numbers are very hard to see in this image. Please enlarge.

Ok

Line 241 – “mineral” – which mineral(s)?

As these are images from reflected light microscopy, we can not distinguish different *minerals.*

Figure 7 – A statement about the white line in this figure may be useful here. Such as, "the white line indicates the outermost rim of the fiber" (similar to dashed line in Fig. 9).

Ok

Figure 9 – Lines 316 and 317 “Areas rich in N are poor in O” – This is not immediately obvious (to me) at first glance. Perhaps some arrows would help here.

Ok

Figure 10 – Line 325 “absent in this area” – is the area rich in S and N on the left side of the images also epoxy, or is it the interior of the OM flake? It is unclear from the images alone. Please clarify (in BSE image or caption)

Will be clarified in the BSE image.

Line 365 – omit “a”

Lines 406 and 407 – “it will be done in a companion paper, also with more details on the spherical objects of OM.” – Has this paper already been submitted or will be published? If so, please refer to the paper as "in review" or “in press”. Otherwise this sentence should be omitted, or replaced with something like "more research is needed to clarify the nature (i.e., biological affinity) of the fossils."

See comment above to line 162.

Lines 416 and 417 – “high degree of aromatization, which relates to high thermal maturity.” – There is extensive literature on the relationship of aromatization and thermal maturity. Please cite such studies here.

Ok, see comment to line 93.

Line 429 – change “ ” to “~”

Ok

Lines 438–444 – Are there other examples in the literature re: porosity as degassing features, or cracks as shrinking phenomena? If so, please cite them here

We are not aware of other studies, so it is our interpretation and we will make it clear in *the revision.*

Lines 482 and 483 – "their Fig. 2" not necessary. It is sufficient to direct reader to Gorlenko et al. (2000).

Ok

Line 493 – “anoxic” – Anoxic refers to an environmental parameter. Suggest change to "anaerobic" if referring to biological characteristic.

Ok, we agree and change to: The miarolitic cavities of the granite, possibly with periodical influx of hydrothermal waters, provided the space for a continental deep biosphere, consisting probably of anaerobic, thermophilic and acidophilic microbial species.

Line 494 – “Methanogenic bacteria” – Methanogens are typically considered archaea. Change to "Methanogenic archaea" or more broadly "Methanogenic microbes".

Ok, we will change into “methanogenic microbes”.

Figure 10 – Line 501 – “three morphologically different organisms (fibrous, flaky, and rare…)” – the different textures do not necessarily refer to different organisms. This terminology should be changed; rather than "organisms" it would be more appropriate to say "OM textures".

For example, the flaky OM could possibly be remnants of altered biofilms (as discussed below in Line 509), rather than a distinct microbial population.

Ok, we can change into OM textures.

Line 511 – “sufficiently low” – How low is "sufficiently low"? Below boiling (i.e., < ~100 C)?

This should be clear from the text, “sufficiently low that organisms can live in this environment”. Thermophylic microorganisms are reported from more than 100 °C.

Line 563 – Suggest change from “Anaerobic” to “Anoxic”

Ok

Lines 571 and 572 – “whereas silicification, when rapid, helps to preserve their morphological details” – Many studies have documented the role of rapid silicification in microbial fossilization, please cite some of them here. (e.g., Bartley, 1996; Manning-Berg et al., 2019 and refs therein, etc.)

Ok

Line 574 – Suggest change from “anaerobic” to “anoxic”

Ok

Line 582 – “continental environment” – It may be worth summarizing what the important differences are here, to aid the reader in understanding why these two environments are significantly distinct for fossilization.

Ok; only in the continental environment, fluids rich in F are present (in the oceanic environment, granites are much less abundant than mafic rocks and they commonly lack F-enriched fluids and typical pegmatites).

Line 599 – "his Fig. 1" not necessary. It is sufficient to direct reader to Zhmur (2003).

Ok

Line 602 – insert "continental" or "subsurface" here (before “localities from marine environments, but this research is unique in that it comes from a terrestrial region.

Ok

Line 604 – Suggest changing “sediments” to “sedimentary rocks”

Ok

Line 604 – Suggest changing “more and more” to “growing”

Ok

Line 609 – “cave” (twice); Not sure if the term "cave" is appropriate here? Perhaps "large water-filled cavity" is better -- at least to avoid confusion with limestone caves in karst environments. (see comment for Line 42.)

Ok, see comment to line 42.