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Interactive comment

Interactive comment on "Sedimentary mechanisms of a modern banded iron formation on Milos Island, Greece" *by* Ernest Chi Fru et al.

A.J.B. Smith (Referee)

bertuss@uj.ac.za

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2017/12/05 Dear Editor – Solid Earth

This letter serves to summarize my review of the manuscript entitled "Sedimentary mechanisms of a modern banded iron formation on Milos Island, Greece", submitted by E Chi Fru et al. for possible publication in Solid Earth.

The manuscript documents Quarternary Fe-rich chemical sediments from the Cape Vani sedimentary basin (CVSB) on Milos Island, Greece. The Fe-rich units show a close associated with Mn-rich units and two subtypes were identified: i) microfossil-rich iron formation (IF); and ii) non-fossiliferous IF. The IFs also occur over a limited lateral extent. Geochemical and mineralogical data suggest that these units are very

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similar to Precambrian IFs and could potentially be proxies to the latter. Depositional conditions are also proposed by the authors, which include tectonics, biological activity, changing redox and abiotic Si precipitation. Although there is some overlap with their previous publications in Nature Communications (2013) and Geobiology (2015), the authors state that a major new addition is presenting plausible mechanisms for the temporal and spatial separation between Fe and Mn deposition in the CVSB.

It must be noted upfront that this manuscript covers a fascinating and important geological occurrence, namely a Quarternary, spatially limited IF. With the majority of IF deposited during the Precambrian and, more specifically, prior to 2 Ga, this occurrence shows how unique and isolated conditions can drastically influence localized geology. Further documentation and more field descriptions of this occurrence is therefore always welcome in the literature. The authors should also be commended on the level into which they attempt to present a depositional model for the units, something which is often not even attempted in manuscripts on IFs. The inclusions of the importance of faulting and tectonics is also a great addition into the model, something which often cannot be done in detail on older, Precambrian IF occurrences. The authors also take special care to address a multitude of possible paleoenvironmental conditions, looking at the past and comparing it to the present, and should be complimented on such an even-handed approach. The conclusion on the cause for the banding (main conclusion 5) being caused by episodic hydrothermal intensification is also an important one, and one that I believe is also supported by evidence from Precambrian IFs.

My comments and corrections for the manuscript are presented as: main comments (numbered); section specific comments (bulleted); and detailed comments in a pdf copy of the manuscript. Some repetition will be present as the pdf copy contains all of the comments below to a certain degree in addition to more detailed comments such as minor content, spelling and grammar corrections. The authors must also take note that they need to activate the comment tool in Adobe Acrobat to see all the detailed comments in the pdf copy. The eight most important points that I believe require additions or adjustments to this manuscript are the following: 1. There is inconsistent use of element names and symbols in the manuscript (e.g. line 233 uses "iron" and "Mn" in the same line). The authors should be consistent in their use of either names or symbols for elements. Also, the use of hyphens are also inconsistent and should carefully be revised and updated to ensure format and spelling consistency across the manuscript. 2. It is important that the authors include, even if briefly, the detail on how the age constraints of the CVSB were determined somewhere in the geological setting of the manuscript. 3. The results section on geochemistry (section 3.3; line 461 onwards) contains a lot of interspersed petrography and mineralogy, which I believe is inappropriate. I strongly recommend that the two sets of results be clearly separated and presented in their own result sections. This will also require some reshuffling and/or re-editing of figures to properly fit the order and flow of the revised sections. 4. The use of North American Shale Composite (NASC) to normalize the REE data is strange and a bit dated. Most new publications on IFs from the mid-1990s onwards use Post-Archean Australian Shale (PAAS) for IF REE normalization. I would recommend the authors rather use this standard as it would make the data more comparable to other IF publications. In addition, the assessment of true Ce anomalies presented in this paper is also based on Bau and Dulski (1996), wherein they used PAAS as the shale standard for normalization. The Ce anomalies therefore need to be recalculated and replotted using PAAS. I do realize this might not make much of a difference, but for comparative purposes and for accuracy relating to the original publication this should be done. To make the REE assessment in this paper even more complete, the authors should also plot YSN in the REE diagram between Dy and Ho (REY plots) as proposed by Bau and Dulski (1996) to get a more complete pattern and assessment of the REE trends 5. The conclusion that the IFs were deposited in reducing conditions in a redox stratified sea/ocean, as indicated in figure 16 and stated in lines 685 to 687, is not currently convincing for the following reasons: 1) The lack of a Ce anomaly is not a definite indicator of reducing conditions. This can be buffered by excess Fe(II) in the system (see classic Eh-Ph diagrams by Brookins as well as Smith et al., 2013, Economic Geology, v. 108: 111-134). 2) The Ce anomaly calculations appear to have been done using NASC-normalized REE data instead of PAAS-normalized data. Proposed mechanisms for deeper water anoxia is left for very late in the manuscript, hinging on modern analogues (section 4.2.5), making the lead up at times unconvincing. Some of these arguments are also based on the interpretation of geochemical evidence to suggest anoxia, when micro-oxic conditions, in my opinion, cannot be completely ruled out. A more even handed approach regarding the Eh conditions throughout the manuscript, and taking into account the redox buffering effect between Fe2+ and Mn2+, is likely required throughout. Micro-aerophilic bacteria also likely played a larger role than currently suggested by the authors when considering how recently deposition occurred and how deep the water could have been (well below wave base). I do believe the authors have generally done a good job regarding Eh conditions in their depositional model and that all the necessary information is throughout the manuscript, but in my opinion they are only 70% there in making it convincing and even handed. 6. The formation of the granular Fe-rich beds (lines 456-459) is not satisfactorily addressed. There has to be morphological evidence within the granules for the authors to be able to commit to either a sedimentary or supergene formational mechanism. 7. To me, there is some confusion regarding deep ocean anoxia relative to hydrothermal venting in the depositional model (lines 995-999). This needs to be clarified in the discussion and lead up. Was deep water anoxia semi-permanent or did the venting play a role in establishing it? Here it appears that anoxia was semi-permanent, but the motivation needs to be better conveyed in the lead-up. 8. In the final conclusion (lines 1013-1017) the authors state that "Whether the rocks described here are analogues of Precambrian BIFs or not, and whether the proposed formation mechanisms match those that formed the ancient rocks, is opened to debate." The work here have many similarities to proposed Precambrian BIF depositional models (e.g. Smith et al., 2013; Bekker et al., 2010 and depositional models by Klein and Beukes, Beukes and Gutzmer). The authors should comment on this briefly.

Below follows my general, section-specific comments. Abstract âĂć The sentence run-

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ning from lines 37 to 38 should be rephrased. As it is currently written it does not clearly convey the stratigraphic relationship between the Fe- and Mn-rich units. Is the transition to the Mn-rich formation upwards or downwards? I think rephrasing this as two sentences briefly providing the bottom-up stratigraphy would clear this up. âĂć The statements in lines 38 to 41 relating to anoxia might not be completely accurate. Refer to point 6 above. âĂć The summary of depositional conditions in lines 46 to 48 is too vague and brief. The authors need to take a few more lines and properly summarize their proposed depositional model. Introduction The introduction and geological setting is brief, concise and appropriate. Here are some comments/corrections: âĂć The author should start the introduction with a one sentence definition of IFs, mentioning their normal age distribution, and moving the references in line 63 and 64 to the end of the definition sentence. In the current form, the references in the middle of the first sentence clutters it and takes away from the impact of this sentence. If it reads better, the authors can also place the IF definition after the current first sentence. âĂć For line 84, a good reference to add would be Beukes et al., 2016, Episodes v. 39: 285-317. It reviews all the Mn deposits of Africa. âĂć More information needs to be provided on how the age range of the CVSB was determined. âĂć Some minor comments and corrections are noted in the pdf copy. Make sure to address these too. Methodology: The following comments related to section 2 need to be addressed: âĂć It should be stated very early on in the methodology section how many samples were taken, what sample types (lithologies) were taken and the approximate localities of the samples. âĂć The sample preparation subsection (lines 119-125) is insufficient. More detail needs to be provided on how samples were taken, and how they were prepared for the different analyses. The type of mill used is not even mentioned. To refer to previous papers in the manner done here for sample preparation is not sufficient. âĂć Lines 120-121: I am not sure how this fits under the subheading of sample preparation. This will need to be moved and better explained. So yes, it does form the basis for facies analysis, but what was actually done and how? âĂć Raman spectroscopy (lines 132-138 should not be included under the XRD subsection heading (section 2.2.1). âĂć Line 172: The

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abbreviations ICP-ES/MS and XRD have not been defined. Also, AcmeLabs has had its name changed to Bureau Veritas. Where is the lab situated? âĂć Lines 226 to 227: To use North American Shale Composite (NASC) for normalization of BIF data is an older way of doing it. Most of the newer publications use Post-Archean Australian Shale (PAAS). The authors should consider rather normalizing to PAAS for better comparison to recent literature. Results: Here are the main points that need to be addressed in section 3: âĂć Lines 266 to 268 contains repetition from what was stated in line 264. The authors should combine and clean this up to remove the repetition. âĂć Line 292: The term "Sh beds" has not been previously defined. What does it mean? âĂć Line 298: The term "Gcm" has not been previously defined. What does it mean? âĂć Lines 398-400: The bracket started in line 398 is never properly closed. Please do so. âĂć Lines 431-434: The phrase "from a relatively shallow and deeper water setting. . . to a relatively deeper quiet water environment" appears to be contradictory at the start. Some rephrasing is required to improve clarity. âĂć Lines 456-459: The granules associated with supergene formation versus those associated with sedimentary reworking will have very different internal structures. Whole rock geochemistry will also be very different. Why is such data not available? These are two very different formational proposals that should be resolved. âĂć Lines 467-469: The way this sentence is phrased does not read accurately. Why do dramatic fluctuations control the Fe to Si ratio? Seems to be overly obvious and at the same time not supported by evidence, as if the lines between correlation and causality are being blurred. I would strongly recommend that this statement gets rephrased to more accurately represent what the data is actually showing, namely an inverse correlation between Fe and Si, which is to be expected when the two components are the only two major ones in the rock! âĂć Lines 520-523: Here the normalization to NASC becomes problematic. The paper that originally presented to calculations and plot to assess true Ce anomalies (Bau and Dulski, 1996), used PAAS as their shale standard. All the calculations in that paper therefore used PAAS-normalized values and NASC. This alone likely justified why the authors should redo the REE data normalized to PAAS. âĂć Lines 522-523: Depending on the journal's citation format, shouldn't "Bau et al." be "Bau and Dulski"? Discussion Section 4.1 is generally well-written and creates a good depositional framework. Please note, however, some comment below that need to be addressed with regards to this sub-section. Here are the main points that need to be addressed in section 4: âĂć Lines 604-606: I do not believe the conclusion here is completely accurate. One can only state the MFIF deposition preceded the second-stage Mn mineralization. There is no clear evidence that the MFIF and first-stage Mn mineralization was coeval. âĂć Lines 614-615: Please rephrase this so that the clarity is improved. âĂć Lines 615-616: "This uplifting into shallower water event"... Which event is this? The discussion preceding this statement in this paragraph has only been referring to a transgressive (i.e. deepening) event. Please rewrite and restructure where necessary to make this paragraph read better and make more sense. âĂć Lines 651-655: Break this sentence into two shorter ones and do some restructuring that it reads better and the content is clearer. âĂć Lines 663-672: This starting sentence for this paragraph reads like it comes out of nowhere. The authors need to lead into the content of this paragraph much better. Also, I am not convinced that this paragraph belongs in the subsection, as it does not directly relate to mineral paragenesis and also reads like it comes out of nowhere. âĂć Lines 685-687: This statement has a few potential problems. Firstly, the lack of a Ce anomaly is not a definite indicator of reducing conditions. This can be buffered by excess Fe2+ in the system. Secondly, the Ce anomaly calculations appear to have been done using NASC-normalized REE data instead of PAAS-normalized data. At the very least the latter issue has to be resolved, and thereafter a more convincing argument need to be provided for reducing conditions. âĂć Lines 697-699: This one line is not convincing enough as a mechanism for redox stratified depositional environment. I admit that better and more convincing mechanisms are discussed later in the manuscript, but here the line comes over as unconvincing. Maybe note that possible mechanism for redox stratification are discussed in more details later. âĂć Lines 722-729: I am not following the argument in point 3 very well. It requires some rephrasing and rewriting to convey the argument more clearly and concisely. âĂć Lines 722: The authors need to re-evaluate all the statements related to Ce anomalies after recalculating the anomalies to PAAS. âĂć Lines 730-738: For point 4 as well, the argument is not coming through clearly. There also appears to be some structuring and grammatical problems in this paragraph. From what I can follow the argument is probably sound, but I cannot be sure as the paragraph is not well written. âĂć Lines 806-809: Many authors agree with the statement that the lack of organic carbon is not due to metamorphism, but for a different reason. The organic matter is also likely destroyed in Precambrian BIF in a redox reaction with Fe3+, leading to the formation of 13C-depleted siderite and ankerite. This should be briefly addressed. See, for example, Smith et al. (2013, Economic Geology, v. 108:111-134) and references therein. âĂć Lines 832-838: The tectonic and sea level mechanisms for changing redox conditions seem plausible. However, it only truly works when the motivation and mechanism for anoxia during IF deposition are more convincing. See main comment nr 6 above. âĂć Lines 851-853: For interest, also see Smith et al. (2013, Economic Geology, v. 108: 111-134). âĂć Lines 857-858: Rephrase and fix the grammar in this sentence. âĂć Line 876-877: The statement "most likely dependent on prevailing redox conditions" is not yet convincing! The accumulation of Mn could also be buffered by the availability of Fe2+. Conclusions âĂć Lines 990-994: Agreed that this is a feasible mechanism. However, Prevalence of available Fe2+ as a redox buffer should also be considered and addressed. âĂć Lines 995-999: This needs to be clarified in the discussion and lead up. Was deep water anoxia semi-permanent or did the venting play a role in establishing it? Here it appears that anoxia was semi-permanent, but the motivation needs to be better conveyed in the lead-up. âĂć Lines 998-999: What about the chemolithoautotrophs (microaerophilic bacteria)? I am not convinced that one can commit to only the photoferrotrophs with the dataset presented here. Figures âĂć Figure 13: The major element oxides on the x-axis of part A should have their numbers changed to subscripts. âĂć Figure 14: The y-axis of part A should be logarithmic! This is the norm for REE spider diagrams and makes the pattern more comparable to published REE data on IFs. âĂć Figure 14: Newer publications normalize the REE data to PAAS. Part B of the figure, which aims to delin-

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eate true Ce anomalies, was also developed based on PAAS normalization (Bau and Dulski, 1996). I therefore think it would be better to normalize the REE data to PAAS so that better comparisons can be made to literature. Y, normalized to PAAS, should also be included between Dy and Ho (after Bau and Dulski, 1996). The Bau and Dulski (1996) reference should also be added to the caption for figure 14 B.

More detailed comments and minor corrections can be found in a pdf copy of the manuscript that should be made available to the authors. All these minor comments should also be addressed for the next version of the manuscript.

My recommendation as reviewer is that following what I consider moderate revisions and addressing all the issues raised in this report, that the paper be accepted for publication in Solid Earth.

Regards,

Bertus Smith Senior Lecturer Department of Geology University of Johannesburg

Please also note the supplement to this comment:
https://www.solid-earth-discuss.net/se-2017-113/se-2017-113-RC1-supplement.pdf

Interactive comment on Solid Earth Discuss., https://doi.org/10.5194/se-2017-113, 2017.