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Discussions

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

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Reviewer Comments

A.J.B. Smith (Referee) bertuss@uj.ac.za Received and published: 5 December 2017

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.

Reviewer: The manuscript documents Quaternary 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 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 Quaternary, 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.

Response: We thank the reviewer (Dr A.J.B Smith) immensely for the enormous time and effort put in reviewing our manuscript. His attention to detail has transformed both the quality of the complex interpretations, better bringing out the remarkable similarities the enigmatic Milos IF share with the Precambrian BIFs and their implications for understanding the past. Below we address his critical comments point by point. Attached to this document is a PDF file named, supplement, containing the manuscript with the changes requested by the reviews in red.

Point 1

Reviewer: 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.

Response: We have amended the text accordingly.

Point 2

Reviewer: 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.

Response: Age constraints and accompanying references are now given in the introductory paragraph in section 1.1, under the geological setting.

Point 3

Reviewer: 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.

Response: We agree that this might be confusing to the reader and have therefore divided section 3.3 into four independent subsections entitled:

3.3.1 Geochemistry of the individual Fe-rich and Si-rich bands 3.3.2 Mineralogy of the individual Fe-rich and Si-rich bands 3.3.3 Hydrothermal versus continental weathering 3.3.4 Redox reconstruction

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Point 4

Reviewer: 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.

Response: We agree that some recent papers have used PAAS (Post Archean Australian Shale-Taylor and Mclennan 1985) instead of NASC (North American Shale Composite-Gromet et al., 1984) while others use UCC (Multi Element Normalisation-Taylor and Mclennan 1985) and Chondrite-Normalised REE-Thomson 1982), which are all scientifically valid standards. In the case of our study, NASC was used for two main reasons: 1. The NASC normalization maintains data consistency with the REE data published in our previous papers on the Milos IF ((1) Chi Fru, E., Ivarsson, M., Kilias, S.P., Bengtson, S., Belivanova, V., Marone, F., Fortin, D., Broman, C., and Stampanoni, M.: Fossilized iron bacteria reveal a pathway to the origin banded iron formations. Nat. Comm., 4, 2050 DOI: 10.1038/ncomms3050, 2013. (2) Chi Fru, E., Ivarsson, M., Kilias, S.P., Frings, P.J., Hemmingsson, C., Broman, C., Bengtson, S. and Chatzitheodoridis, E.: Biogenicity of an Early Quaternary iron formation, Milos Island, Greece. Geobiology, 13, 225–44, 2015.

2. There are no scientifically demonstrated discrepancies between the PAAS and NASC.

3. Following the instructions given here, data was normalized to PAAS for comparison

with the NASC normalized trends. The results produced the same trend as observed when data are normalized to NASC. See new Figure 14 in the manuscript text, accessible in the attached supplement PDF file. Further explanations are also provided under sections 2.6-2.6.1 in the manuscript supplement text. Reviewer: 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.

Response: Unlike the paper by Bau and Dulski that was focused on REE analysis, the REE analysis performed in this study was conducted specifically to answer specific questions that we had posed, relevant to our study. These include:

1. What are the redox depositional conditions? In this revision, we have instead included a new Figure 13C-D, which provides independent support from iron extraction for the reducing depositional conditions displayed by the lack of Ce anomaly, which is critical to this paper than the REY plots. 2. What was the source of sediments to the basin? By using the Eu anomaly, coupled to the relationship between LREE and HREE, which produces a unique graphical shape for hydrothermal deposits, we could predict the hydrothermal/volcanic source of sediments, supported by the strong presence of volcanic ash in the Fe-rich bands. This information is further supported by other methods such as the chemical index of alternation (CIA), which shows negligible contribution of land-derived weathered sediments to the deposit. 3. In future work we will strive to give more thought to REY plots, especially if they can help resolve pertinent hypotheses for how the Milos IF formed.

Point 5

Reviewer: 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.

Response: We appreciate the detailed insights and agree that although widely used, Ce anomalies have to be interpreted with caution. For this reason, we have analysed the same set of samples by the sequential iron extraction approach; a widely applied proxy for reconstructing Paleo-redox. These data presented in the new Figure 13C-D and supported by the references below and several others in the public literature, confirm the inferred anoxic depositional conditions indicate by the Ce anomalies. Comparative normaliztion with either the PAAS or NASC standards, produced the same outcome, in agreement with the interchageable use of both standards. More information on the analysis can be found under sections 2.6-2.6.1 and in Figure 14.

1. Poulton, S.W., and Canfield, D.E.: Development of a sequential iron extraction procedure for iron: implications for iron partitioning in continentally derived particles. Chem. Geol. 2014, 209–221, 2005. 2. Poulton, S.W. and Canfield, D.E.: Ferruginous conditions: A dominant feature of the ocean through Earth's history. Elements. 7, 107–

112, 2011. Point 6 Reviewer: 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.

Response: This statement resonates with the opinion provided the anonymous reviewer. We have therefore deleted the paragraph regarding GIF.

Point 7

Reviewer: 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.

Response: The new Figure 13C-D, which reports on redox reconstruction by sequential iron extraction, has been discussed extensively in the manuscript. This proxy is perhaps the most widely accepted tool for reconstructing paleoredox depositional conditions (i.e., oxic, anoxic but ferruginous and anoxic but euxinic environments. See references given under point 5 above. The proxy works on the basis that it is capable of delineating the redox conditions in the water column beneath which sediments form. We have discussed a number of procedures in the paper by which this anoxia could have developed in the CVSB. The understanding is that there is a combination of the basin being cut off, either in a crater environment like in the adjacent Kolombo volcano and a combination of hydrothermal activity and CO2 accumulation, creating permanent bottom water anoxia. We have explored all these different pathways in the manuscript. However, what has become more certain with the sequential iron extraction data is that deposition occurred under severe anoxic conditions, which could have been the results of numerous processes. These processes will gradually become evident as our work on this formation expands and as other researchers become genuinely interested in

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sampling and exploring its formation mechanisms.

Geochemical REE evidence has shown that Fe was sourced from hydrothermal fluids, and deposition took place beneath anoxic waters (see above). This combined with geological and mineralogical evidence for example the presence of tridymite etc, in Fe-rich layers of the NFIF), indicate that oxidation of Fe(II) in the NFIF corresponded closely in time with major Basin 3-scale intense, possibly episodic, submarine volcanism and hydrothermal activity. We suggest that submarine volcanism/hydrothermalism were responsible for generating a dynamic Basin 3-scale chemocline separating anoxic/suboxic ferruginous deep waters from oxic shallow waters. This is explained by the notion that seawater redox state in a basin with restricted circulation and intense submarine volcanism/hydrothermalism like Basin 3, may be lowered by an enhanced flux of hydrothermally derived reductants, like reduced Fe and Mn, H2 and even CO2-induced stratification, as discussed extensively for various hydrothermal vent fields in the Hellenic Volcanic Arc. These processes would have overpowered the oxidizing potential of seawater (Bekker et al., 2014).

The oxidation of Fe(II) at and below the chemocline, by microaerophilic chemolithoautotrophs and strict anaerobic photoautotrophic Fe(II) oxidation are favored as potential modes of Fe(III)(oxyhydr)oxide precipitation in the NFIF. However, at the current time, such evidence is lacking for the NFIF. We therefore choose not to delve into speculation. One approach had been to use fossil lipid biomarkers, but consistent with the poor organic content of iron formations, this approach proved not to be very successful. Moreover, unlike the MFIF, the NFIF is microfossil-poor, leaving the question of microbial contribution to the deposition of the NFIF wide-opened. On-going stable Fe isotope analysis may help solve this problem. However, Fe isotopes may not be able to differentiate biological activity from abiological processes, because in some cases both can fractionate Fe equally. Nonetheless, our paper provides an intriguing scenario where Precambrian type-rocks are formed in firmly reconstructed anoxic bottom waters under the modern atmosphere. This is unprecedented. We use a multitude of techniques from REEs, carbon isotopes, Raman analysis, TEM, lipid biomarkers, sequential iron extraction, etc, at a comprehensive scale that is hardly ever seen in one paper, to arrive our conclusions.

Point 8

Reviewer: 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.

Response: Your comment has been included in the conclusion.

References 1. Bekker, A., Planavsky, N., Rasmussen, B., Krapez, B., Hofmann, A., Slack, J., Rouxel, O. and Konhauser, K., 2014. Iron formations: Their origins and implications for ancient seawater chemistry. In Treatise on geochemistry (Vol. 12, pp. 561-628). Elsevier. 2. Brookins, D.G., 1988, Eh-pH diagrams for geochemistry: Berlin, Springer-Verlag, 176 p. 3. Brookins, D.G., 1989, Aqueous geochemistry of rare-earth elements: Reviews in Mineralogy, v. 21, p. 201–225. 4. Konhauser, K., 2007, Introduction to geomicrobiology: Malden, Blackwell, 425 p. 5. Konhauser, K.O., Hamade, T., Raiswell, R., Morris, R.C., Ferris, F.G., Southam, G., and Canfield, D.E., 2002, Could bacteria have formed the Precambrian banded iron formations?: Geology, v. 30, p. 1079–1082. 6. McCollom, T.M., and Shock, E.L., 1997, Geochemical constraints on chemolithoautotrophic metabolism by microorganisms in seafloor hydrothermal systems: Geochimica et Cosmochimica Acta, v. 61, p. 4375–4391. 7. Smith, A.J., Beukes, N.J. and Gutzmer, J., 2013. The composition and depositional environments of Mesoarchean iron formations of the West Rand Group of the Witwatersrand Supergroup, South Africa. Economic Geology, 108(1), pp.111-134. 8. Taylor SR, McLennan SM (1985) The continental crust: its composition and evolution. Black-

well Scientific Publication, Carlton, 312 p. 9. Gromet PL et al., 1984. The “North American shale composite”: Its compilation, major and trace element characteristics. Geochim. Cosmo. Acta 48:2469-2482. 10. Thompson, R.N. (1982) Magmatism of the British Tertiary volcanic province. Scott. J. Geol. 18, 49-107.

Specific Comments:

Abstract Reviewer: The sentence running 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.

Response: Rephrased as suggested.

Reviewer: The statements in lines 38 to 41 relating to anoxia might not be completely accurate. Refer to point 6 above.

Response: The statement relating to anoxia is strongly supported by new evidence provided in Figure 13C, in agreement with the lack of Ce anomaly, as discussed above. Also see the extensive discussion on how such anoxic conditions might develop in the CVSB, based on, on-going modern processes that form anoxia along the Hellenic Volcanic Arc. Please kindly check the cited references as they contain valuable information.

Reviewer: 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.

Response: This sentence is given in two parts. The first sentence summarizes the basic Si mineralogy of the two deposits, while the concluding sentence sums up the findings in this study, which are indeed too complex (involving a number of processes) to be laid out completely in the abstract. To attempt to explain each process and how they are linked together is beyond the scope of the abstract, given their complexity. The abstract has been reformatted to read as: An Early Quaternary shallow submarine hydrothermal iron formation (IF) in the Cape Vani sedimentary basin (CVSB) on Milos Island, Greece, displays banded rhythmicity similar to Precambrian banded iron formation (BIF). Sedimentary and stratigraphic reconstruction, coupled to biogeochemical analysis and micro-nanoscale mineralogical characterization, confirm the Milos IF as a modern BIF analogue. Spatial coverage of the BIF-type rocks in relation to the economic grade Mn ore that brought prominence to the CVSB implicates tectonic activity and changing redox in their deposition. Field-wide stratigraphic and biogeochemical reconstruction demonstrate two temporal and spatially isolated iron deposits in the CVSB with distinct sedimentological character. Petrographic screening suggests the previously described photoferrotrophic-like microfossil-rich IF (MFIF), accumulated on basement andesite in a ∼150 m wide basin, in the SW margin of the basin. A strongly banded non-fossiliferous IF (NFIF) sits on top the Mn-rich sandstones at the transition to the renowned Mn-rich formation, capping the NFIF unit. Geochemical evidence relates the origin of the NFIF to periodic submarine volcanism and water column oxidation of released Fe(II) in conditions apparently predominated by anoxia, similar to the MFIF. Raman spectroscopy pairs hematite-rich grains in the NFIF with relics of a carbonaceous material carrying an average δ13Corg signature of ∼-25‰Ḣowever, a similar δ13Corg signature in the MFIF is not directly coupled to hematite by mineralogy. The NFIF, which post dates large-scale Mn deposition in the CVSB, is composed primarily of amorphous Si (opal-SiO2ÂůnH2O) while crystalline quartz (SiO2) predominates the MFIF. An intricate interaction between tectonic processes, changing redox, biological activity and abiotic Si precipitation are proposed to have collectively formed the unmetamorphosed BIF-type deposits in a shallow submarine volcanic center.

Introduction Reviewer: The introduction and geological setting is brief, concise and appropriate. Here are some comments/corrections:

Reviewer: 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

Response: Sentence restructured as suggested.

Reviewer: 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.

Response: Added as suggested.

Reviewer: More information needs to be provided on how the age range of the CVSB was determined.

Response: The text has been updated to: K-Ar radiometric dating of biotite and amphiboles belonging to the dacitic/andesitic lava domes flooring the CVSB basin gave an Upper Pliocene age of 2.38±0.1 Ma (Fytikas et al., 1986; Stewart and McPhie, 2006). The fossiliferous sandstones/sandy tuffs hosting the Mn-rich deposit, which contain the gastropod mollusk guide fossil, Haustator biplicatus sp. (Bronn, 1831), indicate an Upper Pliocene-Lower Pleistocene age.

Reviewer: Some minor comments and corrections are noted in the pdf copy. Make sure to address these too.

Response. We have made all the corrections suggested in the annotated PDF. The responses are highlighted red in the new text appended in the supplementary document.

Methodology

Reviewer: 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

Response: The cardinal points from where samples were collected are given in the paper, such that any individual can follow this direction to the exact location of sampling. This study shows the sawn rocks and discusses how each representative layer was analysed by a variety of methods. The focus of this study is on the fine textures of these rocks, combined with field survey over the entire 1 Km long basin.

Reviewer: 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.

Response: Samples were sawn to remove weathered surfaces, and chips of rocks were sent to GeoTech Labs, which is a certified commercial laboratory for preparing thin sections. We are not sure what can be said about sawing a rock to remove weathered surfaces, which is why that part of the sentence has been left unchanged. Usually, it is enough to provide information on commercial providers, since they are accredited and certified. The rock polishing is a service provided by GeoTech Labs and can be requested at a fix rate, the details of which are not needed for this paper. Thirdly, the manuscript is over 15000 words. It is correct scientific practice to reference methods that can be obtained from previous publications. This is the practice advised by some of the most influential scientific journals. We have beefed parts of the acid digestion and removed parts as requested. However, the mechanism by which the rocks were pulverized is inconsequential because any mechanism would work as long as it enables the final dissolution of the powder into a liquid phase whose chemical analysis can be analyzed which is where focus is put. XRD analysis was performed directly on the pulverized samples as discussed in the manuscript.

Reviewer: 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?

Response. Line120-Line 121 has been removed as advised to Section 3.1, as an introductory sentence under Lithostratigraphy, where the methodology for facies analysis is described in detail.

Reviewer: Raman spectroscopy (lines 132-138 should not be included under the XRD subsection heading (section 2.2.1).

Response: Corrected.

Reviewer: Line 172: The 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?

Response: Corrected.

Reviewer: 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.

Response: We have provided justification above

Results Reviewer: 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.

Response: Lines 266 to 268 have been deleted.

Reviewer: Line 292: The term "Sh beds" has not been previously defined. What does it mean?

Response: It has been removed and named accordingly as explained in the next comment. This abbreviation, like the one below, is an editing oversight.

Line 298: The term "Gcm" has not been previously defined. What does it mean? Response: All abbreviations relating to lithological successions have been removed and fully spelt out throughout the text. "Sh" has been replaced with "plane-parallellaminated sandstone/sandy tuff", "Gcm" has been replaced with "clast-supported pebble-to-cobble conglomerate".

Reviewer: Lines 398-400: The bracket started in line 398 is never properly closed. Please do so.

Response: Corrected

Reviewer: 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.

Response: The paragraph has been shortened to: The hypothesized deepening of Basin 3 is consistent with the interpretation that active rifting was an important mechanism in the formation of the CVSB (Papanikolaou et al., 1990).

Reviewer: 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.

Response: We have not completed the mineralogical and geochemical description of these rocks. Therefore at the moment the sedimentary reworking vs. supergene origin cannot be deciphered. However, resolving this problem is beyond the scope of the present paper, and it is the subject of a future communication. Therefore, we have removed the reference to GIF, leaving the supergene possibility, because to our best judgment this better fits the geological and macroscopic characteristics of these ironstones.

Reviewer: 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!

Response: Revised as suggested to read:

The laser ablation ICP-MS data further show that dramatic fluctuations in Fe concentrations control the Si to Fe ratio in both types of rocks, despite the thousands of millions of years gap between them. This inverse correlation between Fe and Si is expected because they are the two major elemental components of the rock.

Reviewer: 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

Response: We found no difference by normalizing the data either with NASC or PAAS. However, we maintained the NASC data to maintain consistency with recent publications that have used the NASC standard on the Milos IF. See sections 2.6-2.6.1 in the manuscript. Also see Figure 14.

Reviewer: Lines 522-523: Depending on the journal's citation format, shouldn't "Bau et al." be "Bau and Dulski"?

Response: Corrected.

Discussion Reviewer: 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.

Reponse: Deleted

Reviewer: Lines 614-615: Please rephrase this so that the clarity is improved. 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.

Reponse: This paragraph from line 614-line 619 has been modified to: The deepening of Basin 3 is reflected in the underlying graded conglomerate bed that exhibits an upward fining trend, and transitions into the NFIF. The conglomerate bed may represent rapid deposition during a high-energy event, i.e. storm or mass flow, whereas the fining upwards in the bed is better explained by the depositional mechanism losing energy through time. These high-energy conditions apparently must have ceased during the deposition of the overlying NFIF, where we interpret that increased abundance of finely laminated IF and decreased evidence of storm and/or mass flow reworking reflects deepening conditions. The hypothesized deepening of Basin 3 is consistent with the interpretation that active rifting was occurring during CVSB evolution (Papanikolaou et al., 1990).

Reviewer: Lines 651-655: Break this sentence into two shorter ones and do some restructuring that it reads better and the content is clearer.

Response: The sentence split into two as suggested. However, samples were sawn to remove exposed layers and only the laminated bands for the NFIF were analyzed. Modern sediments from Spathi bay, located Southeast of Milos Island where hydrothermal activity is presently ensuing at 12.5 m below sea level, revealed similar plant lipids as recorded in the Quaternary IF (Fig. 15G).

Reviewer: 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

Response: This paragraph has been deleted.

Reviewer: 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.

Response: We have confirmed the redox conditions using another much accepted method as stated above. And as already stated and shown above, whether NASC or PAAS was used, the outcome was the same.

Reviewer: 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.

Response: We have provided more supportive evidence for seafloor anoxia during deposition of both the NFIF and the MFIF using amore reliable redox proxy. Given that bottom water anoxia would have existed beneath a permanently oxygenated atmosphere, surficial waters column would have been oxidized.

Reviewer: 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.

Response: This response is particularly directed at sedimentologists who according to our experience have attacked our conclusions by proposing that anoxic hydrothermal fluids may have penetrated preformed sediments to form the IF-rich bands as a diagenetic product. However this is impossible, given that reduced hydrothermal fluids in anoxic sediments deprived of light and oxygen, would lack oxidizing power to precipitate iron oxides. The new text reads as:

The reducing depositional conditions do not support sediment diagenesis as an alternative model for explaining the origin of the Milos IF. This is because the oxidation of ferrous Fe supplied in reduced hydrothermal fluids, must interact with a sizeable pool of oxygen, enabling microaerophilic bacteria oxidation of ferrous iron to Fe(III)(oxyhydr)oxides (Johnson et al., 2008). Otherwise, light-controlled photoferrotrophyâĂŤan extremely rare sediment characteristicâĂŤprecipitates Fe oxides in the absence of oxygen in sunlight environments Weber et al., 2006).

Lines 722: The authors need to re-evaluate all the statements related to Ce anomalies after recalculating the anomalies to PAAS

Response: See above for justification with links to revision in the text and Figure 14.

Reviewer: 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

Response: This is equally a comment that has been raised by sedimentologists. But we believe that the paper is clear enough and have deleted this point.

Reviewer: 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.

Response: The text has been updated to include this information:

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Discussion paper

Importantly, prokaryotic biomarkers are suggested to poorly preserve in these young BIF analogues. This raises the possibility that this may provide an important explanation for why lipid biomarkers are yet to be extracted from Precambrian BIFs. Moreover, the data are compatible with the low Corg recorded in BIFs of all ages, suggesting that the low Corg abundance may not be due to metamorphism as often proposed (Bekker et al., 2010) or to Corg oxidation by dissimilatory iron reducing bacteria to form 13C-depleted siderite and ankerite during diagenesis (Johnson et al., 2008; Bekker et al., 2010). The Milos BIF-type rocks are unmetamorphosed and lack iron carbonate, yet have vanishingly low Corg levels similar to the ancient metamorphosed BIFs. However, an alternative possibility is that the iron oxides may have been reduced through biological oxidation of organic carbon, but carbonate saturation was not reached (Smith et al., 2013).

Reviewer: 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

Response: We have provided a strong evidence for anoxia by the sequential iron proxy.

Reviewer: Lines 851-853: For interest, also see Smith et al. (2013, Economic Geology, v. 108: 111-134).

Response: According to the anonymous reviewer comments, we felt that it is better to delete lines 851-853.

Reviewer: Lines 857-858: Rephrase and fix the grammar in this sentence.

Response: corrected

Reviewer: 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+

Response: New evidence has been provided that strongly support reducing depositional conditions of both the NFIF and MFIF.

Conclusions

Reviewer: 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.

Response: Redox depositional conditions are firmly established.

Reviewer: 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.

Response: We have provided plausible mechanisms that can explain the anoxia recorded in this basin in extensive review of redox processes along the entire volcanic arc. However the change from Mn deposition to the NFIF certainly indicates that redox was changing intermittently. This subject has been thoroughly discussed throughout the manuscript and to avoid repetition we have not brought it up again here.

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

Response: Lines 995-999:

We agree and have within the entire text discussed this point, but we have been careful since all endeavours have fallen short to identify their presence in Milos. Any extensive discussion on this topic is highly speculative as stated above. Inasmuch as we want to have this discussion, we feel that it is reasonable to limit it to the available data at hand. However, the similar depositional conditions as MFIF, give us the opportunity to discuss more about photoferrotrophy, as there is some evidence pointing to this. We have searched for characteristic microaerophilic fossils such as the twisted stalks of

Mariprofundus ferrooxydans but found no evidence. This sentence has been changed to read:

The mechanism of formation of the MFIF and NFIF therefore most likely involved exhalative release of reduced hydrothermal/volcanic fluids into a restricted and deoxygenated seafloor water column where the oxidation of reduced Fe to Fe(III)(oxyhydr)oxides occurred, most likely by the activity of photoferrotrophs (Chi Fru et al., 2013). Microaerophilic oxidation of Fe(II) was likely critical, but that remains to be shown.

Please also note the supplement to this comment:
https://www.solid-earth-discuss.net/se-2017-113/se-2017-113-AC2-supplement.pdf

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